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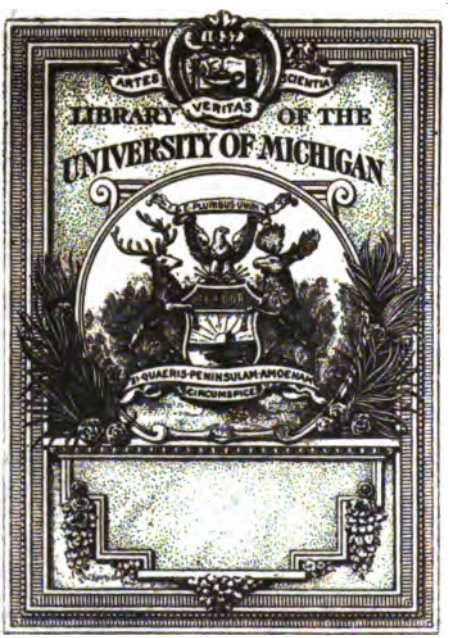
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TRANSACTIONS

OF THE

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VOLUME XI.

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Supt., Willets Manufacturing Company.

GORSLINE, WILLIAM H.,
242 Culver Road,
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Secy. and Mgr., Rochester Sewer Pipe Company.

GRADY, ROBERT F.,
St. Louis, Mo.
Mgr., St. Louis Terra Cotta Co.

GRAHAM, W. A. P.,
New Brighton, Pa.
Secy. and Treas., American Porcelain Company.

GREENER, GEO. COURTRIGHT, E. M., (in Cer.)
63 Chas. Field St.,
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Instructor in Technical High School, Providence, R. I.

GREGORY, M. E.,
Corning, N. Y.
Prop., Corning Brick, Terra Cotta & Tile Company.

GRIFFIN, CARL H.,
Worcester, Mass.
Chemist, The Norton Company.

GRUEBY, WILLIAM H.,
Boston, Mass.
Pres., Gen'l Mgr., Grueby Faience Company.

GUASTAVINO, RAFAEL,
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Pres., The R. Guastavino Company.

HALL, ROBERT T.,
East Liverpool, Ohio.
Secy. and Treas., Hall China Company.

HAMILTON, JAMES,
Trenton, N. J.
Supt., Ideal Pottery of Trenton Potteries Company.

HANSEN, ABEL,
Fords, N. J.
Prop. and Mgr., Fords Terra Cotta & S. Works.

HARDY, ISAAC ERNEST,
Momence, Ill.
Supt., Tiffany Enameled Brick Co.

HARE, ROBERT L.,
Fort Worth, Texas.
Cobb Brick Company.

HARKER, H. N.,
East Liverpool, Ohio.
Gen'l Mgr., Harker Pottery Company.

HARPER, JOHN LYALL,
Niagara Falls, N. Y.
Chief Engineer, Niagara Falls Hydraulic Power & Manufacturing Company.

HARRIS, CHARLES T.,
213 E. 44th St.,
New York City.
J. C. McFarland & Company.

HASBURG, JOHN W.,
244 Lincoln Ave.,
Chicago, Ill.
Pres., John W. Hasburg Company (Inc.)

HASSLACHER, JACOB, 100 William St., New York City. — Pres., The Roessler & Hasslacher Chemical Company.

HASTINGS, FRANCIS N., Hartford, Ct. — Hartford Faience Company.

HAVILAND, PAUL B., 45 Barclay St., New York City. — Haviland & Company.

HAYNES, FRANK R., Baltimore, Md. — Managing Partner, D. F. Haynes & Son.

HENDERSON, H. B., B. Sc., 1538 N. High St., Columbus, Ohio. — Supt., Pyrometric Cone Factory.

HEROLD, JOHN J., Zanesville, Ohio. — Supt., Roseville Pottery Company.

HIGGINS, ALDUS C., Worcester, Mass. — Mgr., Electric Furnace Plant, Norton Company.

HINE, HOMER H., Wellsville, Ohio. — Supt., McLain Fire Brick Company.

HIPP, WM. G., Massillon, Ohio. — Secy. and Gen'l Mgr., Massillon Stone and Fire Brick Company.

HITCHINS, E. S., Olive Hill, Ky. — President, Olive Hill Fire Brick Company.

HOPLER, THORNTON M., Hotel Burdge, Lincoln, Cal.

HULL, W. S., Jackson, Miss. — Architect.

HUMPHREY, DWIGHT ELMER, Cleveland, Ohio. — Deckman-Duty Brick Company.

HURSH, RALPH KENT, Shawnee, Ohio. — The Ohio Mining & Manufacturing Company.

JACQUART, BERNARD, South River, N. J. — Supt., American Encaustic Brick and Tile Company.

JEPPSON, GEORGE N., 286 W. Boylston St., Worcester, Mass. — Asst. Supt., Norton Company.

JUNGE, WILLIAM H., Glenview, Ill. — Northwestern Terra Cotta Company.

JUSTICE, ITHAMAR M., 3305 E. Third St., Dayton, Ohio. — Head of Engineering Department, C. W. Raymond Company.

KANENGEISER, FRED. R., Bessemer, Pa. — Gen'l Supt., Bessemer Limestone Company.

KEELER, R. B.,
918 W. Illinois St.,
Urbana, Ill.

KERR, CHARLES HENRY, — Research Chemist, American Optical Co.
Southbridge, Mass.

KNOTE, JOHN H., M. Sc., — Assistant Professor in Ceramics, University of Illinois.
Champaign, Ill.

KOCH, CHARLES FREDERICK, — Cambridge Tile Mfg. Company.
2407 Highland Ave., Mt. Auburn,
Cincinnati, Ohio.

KOCH, JULIUS J.,
3325 Caroline St., St. Louis, Mo.

KOCH, WILLIAM H., — Superintendent Art Pottery.
Wheeling Ave., Zanesville, Ohio.

KRICK, GEO. M., — Genl. Mgr., Krick, Tyndall & Company.
Decatur, Ind.

LANDERS, WILLIAM FRANKLIN, — Supt., U. S. Encaustic Tile Works.
Indianapolis, Ind.

LANSING, CHARLES W., — Editor "Brick."
45 Plymouth Court, Chicago, Ill.

LAWSHE, C. PERRIN, — Genl. Mgr., Trent Tile Company.
Trenton, N. J.

LAYMAN, FRANK E., E. M., (in Cer.) — Chemist, Cuttler-Hammer Company.
The Aberdeen, Milwaukee, Wis.

LEWIS, EDWIN J.,
Chittenango, N. Y.

LEWIS, THOMAS K., B. Sc., — Assistant Professor, Engineering Drawing, Ohio State University.
Columbus, Ohio.

LINDLEY, JACOB, — Riverside Potteries Company.
Tiltonville, Ohio.

LINDSAY, ROBERT D., — Supt., Denver Pressed Brick Co.
Denver, Colorado.

LINES, EDWIN T., B. Sc., — Illinois Geological Survey.
Urbana, Ill.

LLOYD, HARRY, — Supt. Colonial Clay & Coal Co.
New Salisbury, Ohio.

LOCKE, FREDERICK M., — Manufacturer Porcelain Insulators.
Victor, N. Y.

LOCKE, MORTON FIELD, — Manufacturer Porcelain Insulators.
Lima, N. Y.

MCBEAN, ATHOLL, — Secy., Gladding, McBean & Co.
311 Crocker Bldg.,
San Francisco, Cal.

McNICOL, JOHN A., East Liverpool, Ohio. — Treas., D. E. McNicol Pottery Company.

MADDISON, ERNEST A., 1422 23rd Ave., South Seattle, Wash.

MADDOCK, ARCHIBALD M., Trenton, N. J. — Thomas Maddock & Sons.

MADDOCK, JOHN, Trenton, N. J. — John Maddock & Sons.

MALM, ARTHUR T., CR. E., 18 Orme St., Worcester, Mass. — Ceramic Engineer, Norton Co.

MANDLE, I., Wright Bldg., St. Louis, Mo. — Secy. and Treas., Mandle-Sant Clay Company.

MANDLE, SIDNEY, Wright Bldg., St. Louis, Mo. — Asst. Treas., The Mandle-Sant Clay Company.

MANOR, JNO. M., East Liverpool, Ohio. — Mgr., The Golding Sons Company.

MASON, FORTUNATUS Q., East Liverpool, Ohio. — Color Manufacturer.

MAYER, ARTHUR ELLIS, Beaver Falls, Pa. — With Mayer Pottery Company, Ltd.

MEAKIN, ROBERT J., East Liverpool, Ohio. — Mgr., Hall China Co.

MELLOR, F. G., Trenton, N. J. — Genl. Mgr., Cook Pottery Company.

MERRY, CARL E., Streator, Ill. — Barr Clay Company.

METZNER, OTTO, Cincinnati, Ohio. — Supt. of Manufacture, Rookwood Pottery Company.

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MILES, JAMES, 1072 Penn Ave., East End, East Liverpool, Ohio.

MITCHELL, WALTER CHARLES, 824 Chamber of Commerce, Portland, Oregon. — Resident Agent, Denny-Renton Clay & Coal Company.

MONTGOMERY, E. T., E. M. (in Cer.) Trenton, N. J. — Supt. Elec. Insulator Co. for H. T. Paiste Co.

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MOREY, D. F., Mgr., Ottumwa Press Brick & Coal Company.
Ottumwa, Iowa.

MORRIS, WILLIAM C., Pres., Laclede-Christy Clay Products Company.
St. Louis, Mo.

MOSES, JAMES, Mercer Pottery Company.
Trenton, N. J.

MOULTON, D. A.,
Ironton, Ohio.

MUNSHAW, LAMBERT M., Ceramist, American Terra Cotta & Ceramic Company.
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OUDIN, CHARLES P., Mgr., American Fire Brick Co.
1323 3rd Ave., Spokane, Wash.

PATTERSON, J. W., Mgr., Patterson & Son, Yellowware Potters.
Anderson Ave., Wellsville, Ohio.

PETERSON, RUDOLPH A., "Chemicals & Oils."
108 Fulton St., New York City.

PFEIFFER, JACOB, Pres., Logan Clay Products Co.
718 Bryden Road,
Columbus, Ohio.

PHILLIPS, WILLIAM, Supt., N. Clark & Sons.
609 Haight Ave., Alameda, Cal.

PITCAIRN, WILLIAM S., Importer of China and Earthenware.
44 Murray St., New York City.

PITZER, N. G.,
Cherryvale, Kansas.

PLUSCH, HERMAN A., B. Sc., Chief Ceramic Chemist, Atlantic Terra Cotta Company.
Perth Amboy, N. J.

PODMORE, JOSEPH, Asst. Supt., Ostrander Fire Brick Company.
309 2nd St., Troy, N. Y.

POOLE, JOSHUA, Mgr., Homer Laughlin China Company.
East Liverpool, Ohio.

PORTER, ALFRED S., Sales Mgr. Kenilworth Tile Co.
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POST, MALCOLM P., Supt., Minneapolis Sewer Pipe Works
4429 Thomas Ave.,
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POWELL, WILLIAM H., Pres., Atlantic Terra Cotta Co.
200 W. 70th St., New York City.

PRESTON, FRANCIS C., Vice Pres. and Sales Mgr., Dover
Cuyahoga Bldg., Cleveland, Ohio. Fire Brick Company.

PRICE, F. N., Genl. Mgr., Electric Porcelain &
315 Monmouth St., Manufacturing Company.
Trenton, N. J.

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Mt. Savage, Md.

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Indianapolis, Ind.

RANDALL, THEODORE A., Editor, "Clayworker."
Indianapolis, Ind.

REA, WILLIAM J., Supt., Buffalo Pottery Company.
Buffalo, N. Y.

REYNOLDS, PIERCE B., Asst. Supt., Denny-Renton Clay &
Van Asselts Sta., Seattle, Wash. Coal Company.

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Oyster Bay, L. I., N. Y.

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RITTER, A. G. VAN BRIGGLE, Pres. and Art Director, The Van
Colorado Springs, Colo. Briggle Pottery Company.

RIVERS, WILLIAM EDWARD, Vice Pres., Old Bridge Enameled
Old Bridge, N. J. Brick Company.

ROBINEAU, S., Pres., Keramic Studio Publishing
108 Pearl St., Syracuse, N. Y. Company.

ROBINSON, EDWARD WANTON, Genl. Mgr., Hartford Faience Co.
Hartford, Ct.

RODGERS, EBEN, Secy. and Treas., Alton Brick Co.
Alton, Ill.

ROESSLER, FRANZ,
39 High St., Perth Amboy, N. J.

ROGERS, GREGORY L., Ass't Supt., Thornton Fire Brick Co.
Grafton, W. Va.

ROWE, JOHN, Asst. Supt., American Encaustic Tiling Company.
Zanesville, Ohio.

SANT, JOHN, Clay Salesman, Miner and Broker.
East Liverpool, Ohio.

SANT, THOMAS HERBERT, Clay Salesman, Miner and Broker.
East Liverpool, Ohio.

SAUEREISEN, FRED, Supt., Porcelain Dept., Nernst Lamp Company.
Pittsburgh, Pa.

SAVAGE, HARLOW DOW, Treas., Ashland Fire Brick Co.
Ashland, Ky.

SHAW, JOSEPH BRADFIELD, CE. E., Enameler, Grand Rapids Refrigerator Company.
Grand Rapids, Mich.

SIMPKINS, RALPH, Mgr., Union Pressed Brick Co.
St. Louis, Mo.

SINCLAIR, HERBERT, Genl. Mgr., Star Porcelain Co.
Trenton, N. J.

SINGER, L. P., Chemist, Gladding, McBean & Co.
Lincoln, Cal.

SMITH, AMEDEE M., Pres., Western Clay Mfg. Company.
515 Beck Bldg.,
Portland, Oregon.

SMITH, HARRY W., Representative, Roessler & Hasslacher Chemical Company.
314 Smith St.,
East Liverpool, Ohio.

SMITH, PERRY A., Secy., A. F. Smith Company.
New Brighton, Pa.

SMITH, RAYMOND R., Student, Ceramic Dept., University of Illinois.
410 E. Green St.,
Champaign, Ill.

SPEIR, HARRY F., Supt., Pennsylvania Pulverizing Company.
Lewistown, Pa.

STALEY, HOMER FRANCIS, A. B., Supt., The McCrum-Howell Company.
Uniontown, Pa.

STAMM, JOHN, Supt., National China Company.
859 Ohio Ave.,
East Liverpool, Ohio.

*STANBERY, GEORGE A., Manager, American Encaustic Tiling Company, Ltd.
Zanesville, Ohio.

*Died March 23, 1909.

STEVENSON, WILLIAM G., East Liverpool, Ohio. — Genl. Mgr., Ohio Silica Company.

STOWE, CHARLES BROWN, Cleveland, Ohio. — Pres., National Fire Brick Company.

STULL, RAY THOMAS, E. M. (in Cer.) Urbana, Ill. — Asst. Professor of Ceramics, University of Illinois.

TAKAHASHI, KAKUICHIRO, CE. E., Clarksburg, W. Va. — Chemist, Hazel Atlas Glass Co.

TAYLOR, WILLIAM WATTS, Cincinnati, Ohio. — Pres., Rookwood Pottery Co.

THOMAS, CHAUNCEY RAPELJE, 95 D. University of Chicago, Chicago, Ill. — Teacher, School of Education, University of Chicago.

THOMAS, DAVID C., Minerva, Ohio. — Ceramic Chemist and Head Burner, Owen China Company.

THOMAS, GEORGE W., East Liverpool, Ohio. — Pres. and Genl. Mgr., The R. Thomas & Sons Company.

THRALL, CHARLES U., Tottenville, S. I., N. Y. — Supt., Atlantic Terra Cotta Company.

TONE, FRANK J., Niagara Falls, N. Y. — Works Mgr., Carborundum Company.

TOPPING, J. A., 95 1st Ave., Columbus, Ohio. — Mgr., Sales., Columbus & Hocking Coal & Iron Company.

TOWNSEND, EVERETT, 344 Bellevue Ave., Trenton, N. J. — Genl. Mgr., Robertson Art Tile Company.

TROMMER, CARL E., 319 E. 57th St., New York City.

TURNER, JAMES, 314 Cayuga St., Syracuse, N. Y. — Supt., Iroquois China Company.

VEIOCK, ALBERT, Monmouth, Ill. — Supt., Monmouth Mining & Mfg. Company.

VODREY, WILLIAM E., East Liverpool, Ohio. — Genl. Mgr., Vodrey Pottery Company.

VOLZ, WILLIAM J., St. Louis, Mo. — Supt., Evens & Howard Fire Brick Company.

WAGNER, FRITZ, 1000 Clybourn Ave., Chicago, Ill. — Vice Pres. and Treas., The Northwestern Terra Cotta Company.

WALCOTT, BENJ. D., Indianapolis, Ind. — Pres., Indianapolis Terra Cotta Company.

WANKA, LOUIS,
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Supt., Terra Cotta Department, Washington Brick, Lime & Mfg. Company.

WELLINGTON, ARTHUR J.,
235 Franklin St., Boston, Mass.
Richmond Brick Company.

WELLS, HARRY B.,
South Webster, Ohio.
Supt., The South Webster Brick Company.

WEST, HARRY HYDE,
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Chemist.

WHEAT, HOWARD I.,
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Asst. Supt., Chestnut Ridge White Brick Company.

WHITEHEAD, C. LOUIS,
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Pres., Providential Tile Company.

WHITMER, J. D., CE. E.,
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Chemist with Pacific Face Brick Company.

WHITTAKER, JOHN L.,
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Works Mgr., Lenox, Incorporated.

WILL, OTTO W.,
Perth Amboy, N. J.
Supt., Color Dept., Roessler & Hasslacher Chemical Company.

WILLIAMS, IRA A., M. Sc.,
Ames, Iowa.
Associate Professor, Geology and Mining Engineering, Iowa State College.

WIRT, HERBERT C.,
Burrage, Mass.
Pres., Wirt Mfg. Company.

WORCESTER, WOLSEY G.,
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WORTH, S. HARRY,
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Philadelphia, Pa.
Pres., Pennsylvania Feldspar Company.

YATES, ALFRED,
Shawmut, Elk Co., Pa.
Gen'l Mgr., Shawmut Paving Brick Company.

YOUNG, GEORGE F.,
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Mgr., Roseville Pottery Company.

*ZIMMERMAN, CLARENCE IRVING,
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Madison, Wis.
Graduate Student, University of Wisconsin.

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*Died May 15, 1909.

ANNUAL REPORT OF THE BOARD OF TRUSTEES.

ROCHESTER, N. Y., February 1, 1909.

To the Members and Associates of The American Ceramic Society:

We take pleasure in submitting to you the Eleventh Annual Report of the Society, for the period beginning February 1, 1908, and ending February 1, 1909.

VOLUME X.

Volume X constitutes a notable addition to the literature published by the Society. It contains 582 pages, which is considerably less than Volume IX, but this is not due to a deficiency of matter which the Society could have had for publication, but to the financial ability to pay for its publication. For the first time, the Board regulated its publication by the cost, rather than the supply of matter.

The volume is a step ahead in most respects other than mere size. Mechanically, it is greatly improved by the use of a dense, finely-finished book paper, in place of the soft pulpy paper of the earlier issues. This paper has cost a little more, but this has been partly made up by the reduced cost of half-tone illustrations which did not have to be printed separately and tipped in by hand, as heretofore.

In the binding also, the experiment of putting out part of the issue in cloth covers has worked out very satisfactorily. The members have shown that they like the new dress of the volume, by paying the extra tax of 50 cents per copy for it in large numbers, and the public are certainly more pleased with it, as it puts the work in a permanent, durable and sightly form, so that the small added cost seems more than justified, and the Board recommends that the practice of binding a part of the issue be continued for the ensuing year. At the same time, members in paying their dues should specify which binding they prefer and include the additional 50 cents if they desire the bound copy.

In the time required for publication, this year has witnessed some improvement. It is, however, only to be regarded as a partial return to propriety, from which we had lapsed most seriously for several years before. As the editor most justly says in his preface: "The volume ought to be in the hands of the members within four months after our annual meeting", and it is hoped that this result may be secured another year with the experience now at hand as a guide. If the editor can begin promptly after

the meeting and devote his time and energy to the task, it seems not improbable that June or July at the latest will see the volume out.

The employment of a regular paid editor, and no longer leaving the formidable task of preparing the annual volume to the gratuitous efforts of the Secretary, is the greatest step made in recent years in our internal management. The Board did not decide to take this step until April 15th, on account of the financial risk involved in contracting to pay the Editor's salary, but as the Secretary was absolutely unable to undertake the work again this year, the step became a necessary one and the results have proved advantageous in every direction. As will be seen later, this step has not resulted in a deficit.

In the choice of an Editor, the Board congratulates itself and the Society. Mr. W. D. Richardson has given the work his very best care and attention and has brought to the task a wide knowledge of the literature of clay manufacture.

In the general character and tone of the articles composing the volume, the Board thinks that there has been at least no falling off, and some compliments have been received from our foreign co-workers on the unusual value of the volume.

THE FINANCIAL STATEMENT.

The statement following is a balance of the books of the Society for the year February 1, 1908, to February 1, 1909.

DEBITS.

Brought forward from preceding year		$112.24
FROM DUES AND INITIATION FEES.		
249 associates for 1908 @ $4.00	$996.00	
1 associate for 1908 @ $3.00 (partly prepaid in '07)	3.00	
58 associate initiation fees for 1908 @ $5.00	290.00	
3 associate dues for 1909 @ $4.00 (paid in advance)	12.00	
4 associate fees for 1909 @ $5.00	20.00	
49 members dues for 1908 @ $5.00	245.00	
1 members dues for 1909 @ $5.00 + foreign exchange	5.13	
3 members initiation fees for 1908 @ $5.00	15.00	
8 associate dues 1907 @ $4.00	32.00	
3 associate fees 1907 @ $5.00	15.00	
		$1,633.13
Book Binding Fund		79.65

FROM SALE OF PUBLICATIONS.

Volume I	25	
Volume II	25	
Volume III	25	
Volume IV	23	
Volume V	32	
Volume VI	27	
Volume VII	30	
Volume VIII	28	
Volume IX	36	
Volume X	32	
Manual	87	915.41
Branner Bibliography	53	102.93
Seger's Collected Writings, Vol I	12	
Seger's Collected Writings, Vol. II	11	172.50
Total		$3,015.86

CREDITS.

Cost of Publishing Volume X —

Stenographic Report	$200.00	
Illustrations, Drawings and Engravings	312.60	
Printing, Binding and Casing	808.97	
Editor's salary, 10 months @ $60 per month	600.00	
		$1,921.57
Money advanced on stenographic report of Volume XI		60.00

Cost of Collected Writings of Seger —

Paid to Chemical Publishing Co., @ $10.59 per set for 11½ sets	121.82	121.82

Cost of Running Secretary's Office —

Salary of Assistant Secretary	199.92	
Postage, Stationary and Supplies	142.54	
Expressage of volumes	58.90	
Convention Circulars, Notices, etc	30.57	
Telegrams	3.08	
Insurance on Transactions	10.00	
Labor	1.20	
		446.21
Cost of binding extra sets of volumes		30.15

Amount outstanding for Transactions which cannot be collected	42.44	
Amount outstanding for dues	99.00	
Amount outstanding for Transactions	27.60	
Amount oustanding for Branner Bibliography	14.16	
Amount outstanding for Manual	.80	
		184.00
Cash on hand		252.11
Total		$3,015.86

This statement shows a number of very interesting things. The principal or most important fact is that in spite of the very low state of our treasury on February 1, 1908, and the outlay of $600.00 for the Editor's salary, there has been no deficit created and we have a very comfortable increase in our balance in bank. The actual increase in earnings for this year has been about $860.00. This has been due to: *First.* The limitation of the cost of Volume X, by limiting the material printed. *Second.* The entire extra cost of binding a part of the issue in cloth has been virtually assessed on the members and others who have already bought the volume in that form, so that we have not cut into our income for this experiment. *Third.* The prompt response to the Secretary's appeal for aid in increasing the membership, and the sales of our literature. The number of applications for associate membership received in response to this call has been not less than 33, and the sale of volumes since that time has amounted to over $480.00, or about 40% of the total business of the year. *Fourth.* The Board has also countenanced a new procedure regarding new members, which will be described fully later in the report. By this procedure, the current year's receipts have been much improved, and a number of handsome sales of Transactions at members' rates have been made.

The outlook for the ensuing year, from the financial standpoint is encouraging. The situation should be no worse than last year, and a slightly larger membership list should help us somewhat.

PUBLICATIONS.

The annual inventory of the publications is as follows:

	Remaining on hand Feb. 1, 1908.	Received Since.	Disposed of since, by sale or otherwise.	In stock, according to books.	Actual Inventory.
Volume I	248		25	223	223
Volume II	234		25	209	211
Volume III	242		25	217	217
Volume IV	208		23	185	187
Volume V	187		32	155	155
Volume VI	212		27	185	184
Volume VII	219		30	189	187
Volume VIII	208		28	180	179
Volume IX	220		36	150	152
Volume X		548	338*	210	208
Manual	97		88†	9	9
Branner Bib.	910		52	858	859
	2,985	548	729	2,770	2,771

*29 copies for Library of Congress, exchange list, and complimentary.
†1 copy for desk use.

The heavy sale of volumes this year has cut into our stock of literature very considerably, notwithstanding the fact that we printed a larger issue of the annual volume than heretofore. This shrinkage in stock amounts to 214 volumes, and leaves us only 1904 volumes of the Transactions, when the Branner Bibliography and the Manual are excluded.

On consulting this table, you will see that 6 of our 10 volumes are now down below the 200 mark and have been advanced in price in accordance with the legislation adopted at the Seventh Meeting, and two of them are almost down to 150 copies, when they will become liable for their second advance in price. This month will probably see the last of the Manuals of Ceramic Calculation sold, and the sole remaining source of this booklet will then be Volume II, which will probably be used up rapidly for that reason.

Regarding the Branner Bibliography, we would say that strenuous efforts have been made this year to sell this volume, and as a result 52 copies have been marketed. This has involved the sending out of two sets

of circulars to some 700 libraries. The sales resulting from these circulars have been more than enough to cover cost for printing and postage, of course, but not nearly as many as have been sold by private correspondence and to members of the Society. Efforts have been made recently to arrange for the sale of the whole edition outright to some book dealer who could market the book to better advantage than we can do, and negotiations in that direction are still in progress.

The sale of the Collected Writings of Seger still continues. We have a small but fairly steady income from this source each year and this year it has been increased instead of showing signs of falling off.

These volumes are kept carefully stored in a room for this purpose only, and under lock and key. They are insured in the sum of $2,000.00. Their value at the rate of $3.00 each for the volumes, $1.00 each for the Branner Bibliographies and Manuals, foots up $6,579.00. The lower valuation of the Bibliographies is made on the idea that the entire issue will not bring the present price, owing to its limited market.

GROWTH IN MEMBERSHIP.

The year has been a prosperous one, and our membership stands at its highest level at the present time.

The statistics are as follows:

Brought forward February 1, 1908 —		
Honorary members	2	2
Full members, resident	46	
foreign	1	47
Associate members, resident	185	
foreign	22	207
Total		256
Accessions During Year —		
By election to full membership, resident	1	
foreign	2	3
By election to associate membership, resident	57	
foreign	2	59
Total		62
Losses During Year —		
By death — associate members, resident	1	
foreign	1	2
By resignation — associate members, resident	2	2
By non-payment of dues, associate members	10	10
By promotion to full membership	1	1
Total		15

Present Status —		
Honorary members	2	2
Full members, resident	47	
foreign	3	50
Associate members, resident	225	
foreign	26	251
Total		303

We have a net gain in membership of 54, or 21%. This fine showing is the more remarkable when we consider that the percentage is calculated on the enrollment of 1908 as a basis, the largest heretofore reached. Of this enrollment, the great gain has been in associate membership, and the percentage distribution of full and associate members now stands at 16.1% and 83.2.

This large increase in membership has partly been brought about by a change in our procedure, — all who have applied for associate membership, on properly prepared blanks, and who have paid their fees and dues in advance, have been given the option of coming in at once as provisional members, pending the formality of election, and have been placed on our rolls and been furnished the volume of the Transactions for the current year. Twenty-one have availed themselves of this opportunity. Other applicants, who have not paid in advance, or who having paid in advance have expressed a desire to have their election apply for the coming year, have been held over for addition to the rolls as members of 1909. The growing appreciation of our organization abroad, as evidenced by the considerable foreign list, is a source of much satisfaction to the Board.

THE UNITED STATES GEOLOGICAL SURVEY.

The records of the various and continued efforts of this Society to enter into closer relation with the several state geological surveys and the United States Geological Survey have been recorded in our previous reports. It is a source of much pleasure to the Board to be able to announce that these efforts have not been in vain, and that they have been of more or less assistance to two or more State Surveys in undertaking the study of clays and the clay industries in the current year. In addition, the United States Geological Survey has proceeded to establish in its Technologic Branch at Pittsburg, a Ceramic Department, full fledged and well equipped for research in our field, and it has honored this organization by selecting as the head of this department, no less a person than our own honored presiding officer, and as his staff, two other members of the Society. The instrumentality of this organization in bringing this happy and auspicious event to pass cannot be doubted — indeed, it is a confessed fact by the Survey officials. This event marks the beginning of a new era in American Ceramic Engineering. At last we have a bureau, well equipped for

research, under the skillful management of one of the most scholarly and thoro ceramists, with a corps of capable assistants, and surrounded by other bureaus for research in kindred subjects, all backed by the power and prestige of the national government. While we as individuals owe it to ourselves to still strive as we have heretofore striven, to produce annually some contribution to our profession, we may now confidently look forward to the solution of many important problems of ceramic technology, which we as individuals could never alone have undertaken. No event of such significance to our work has occurred since the organization of this Society itself.

SUMMER MEETING.

The unfortunate failure of the effort made by the Secretary to arrange a Summer Meeting in Colorado is fresh in the minds of all, and also the unsuccessful attempt to secure a committee to organize a meeting in the east later in the summer. This problem is one of long standing and of much importance. The Board desires the Society to seriously consider what our policy in this matter should be and what steps can be taken to make summer meetings a success, if any are to be held. The appointment of a committee at each annual meeting, charged to organize a meeting in a designated locality in the ensuing summer, might perhaps do much to make the occasion more successful.

CONTRIBUTING MEMBERSHIP.

Last year a plan was formulated after some discussion, looking to the increase of our revenues by the creation of a new class of members to be called contributing members. Authority was given the Board to put this plan into effect during the year, if they considered it necessary. The purpose of the extra sums thus raised was to secure as a paid Editor, a capable and well trained ceramist who should in time become the Secretary of the Society and give his whole time and attention to its affairs.

The financial condition of the country was so unsatisfactory during the whole of the preceding year and has been so unsettled and business in the clay industries has in general been so poor, that the Board, after printing up the necessary pledges and blanks and a carefully prepared statement of the whole plan, decided not to put the literature out until times should become better. The employment of an Editor, to give a part of his time to the Society in the preparation and printing of Volume X, and the hope of being able to pay him from the regular revenues of the Society, without the use of the new mode of securing funds was finally decided on, and has fortunately been carried thru with no loss and a slight gain. This does not at all change the situation as to the needs of more income and the dominating importance of securing a permanent paid Secretary — it has merely permitted the matter to stand in abeyance for a time.

ASSISTANT SECRETARY.

The work of looking after the routine correspondence, the book-keeping, the sales of literature, and preparing data for reports, etc., has grown steadily in recent years. For this work the Society has been allowing the Secretary the sum of $200.00 per annum for stenographic assistance for several years past, but with the growth in the commercial side of the Society's business, the sum is not adequate. Further, the work done for this money is of a much higher grade than mere stenography. The Secretary has asked that the Society create the office of Assistant Secretary, and that the compensation for this work shall be $300.00 per annum. The position of Assistant Secretary not to be an elective office, but shall be filled by appointment by the Secretary, with the consent of the Board.

The Board has decided to grant this request, so far as the financial part is concerned and refers to the Society the question of the office and title.

THE OUTLOOK.

With increased membership, with no debts and a small balance in the treasury, with a fruitful session about to begin, with an increasing recognition and respect among clay-workers and others for the sayings and doings of this body, and with the inspiration and aid of the new government bureau in correlating ceramic research, it seems indeed certain that the coming year will be a most fruitful one and that there will be no halting in our forward march.

THE BOARD OF TRUSTEES,
BY EDWARD ORTON, JR., *Secy.*

TREASURER'S REPORT FOR THE YEAR ENDING JAN. 30, 1909.

RECEIPTS.

To balance from previous report	$112.24	
To February collections	280.55	
To March collections	217.98	
To April collections	542.10	
To May and June collections	244.30	
To July collections	204.61	
To September collections	134.07	
To October collections	163.53	
To November collections	499.51	
To December collections	66.76	
To January collections	385.80	
Total for the year		$2,851.45

EXPENDITURES.

By vouchers attached	$2,049.34	
By vouchers issued but not presented for payment, viz:		
Jan. 23, Hann & Adair Printing Co	14.05	
Jan. 23, North Am. Supply Co	4.00	
Jan. 23, Mrs. Kalb	66.50	
Jan. 23, Chemical Publishing Co	10.64	
Jan. 23, M. L. Seymour	16.66	
Jan. 23, W. D. Richardson	60.00	
Jan. 28, O. S. U. Chem. Supply Store	1.62	
Jan. 28, Hann & Adair Printing Co	308.97	
Jan. 28, Hann & Adair Printing Co	4.50	
Jan. 28, W. D. Richardson	60.00	
Jan. 28, Geo. R. Mumma	.60	
Jan. 28, C. E. Henderson	.60	
Jan. 23, American Express Co	1.86	
		2,599.34
By bank balance		252.11
		2,851.45

Bank balance per book attached	$802.11	
Vouchers issued but not presented for payment per above list	550.00	
Net balance	$252.11	

Also are attached vouchers completing last report, as follows: Am. Ex. Co., $1.85; Chem. Pub. Co., $5.32; M. L. Seymour, $16.66, making a total of $23.83.

Respectfully submitted,

ELLIS LOVEJOY, *Treasurer.*

RULES.

OBJECTS.

The objects of the American Ceramic Society are to promote the arts and sciences connected with Ceramics by means of meetings for social intercourse, for the reading and discussion of professional papers, and for the publication of professional literature.

MEMBERSHIP.

The Society shall consist of Honorary Members, Members and Associates.

Honorary Members must be persons of acknowledged professional eminence, and shall not exceed five in number.

Members shall be persons competent to fill responsible positions in Ceramics and have suitable qualifications.

Associates shall include persons interested in Ceramics and the allied arts.

Honorary Members shall be proposed by at least five members, approved by the Board of Trustees, and receive at least 90 per cent of the votes cast by letter ballot at the annual meeting.

Members and Associates shall be proposed by at least three Members or Associates, approved by the Board of Trustees, and receive at least 75 per cent of the votes cast by letter ballot. A candidate for admission must make application on a form prepared by the Board of Trustees which shall contain a written statement of his age, professional experience, and that he will, if elected, conform to the laws, rules, and requirements of the Society.

All Honorary Members, Members and Associates shall be equally entitled to the privileges of membership, except that only Members shall be entitled to hold office and to vote. Applicants for a change in grade of membership shall conform to the requirements of a new applicant.

Any person can be stricken from the membership of the Society on the request of five or more members, on the recommendation of a majority of the Board of Trustees, if he fails to resign on the advice of the Board of Trustees. Such person, however, shall be first notified of the charges against him, and be given a reasonable time to appear before the Board of Trustees, or present written defense, before final action is taken by the Board of Trustees.

DUES.

Honorary Members shall be exempt from all dues.

The initiation fee of Members shall be ten dollars, and of Associates five dollars, which if not paid within six months after election, will render the election void.

The annual dues for Members shall be fixed by the Board of Trustees, but shall not exceed five dollars per year.

The annual dues for Associates will be fixed by the Board of Trustees, but shall not exceed four dollars per year.

Any Member or Associate in arrears for over one year may be suspended from membership by the Board of Trustees until such arrears are paid.

OFFICERS.

The affairs of the Society shall be managed by the Board of Trustees, consisting of a President, Vice President, Secretary, Treasurer, and three Trustees, who shall be elected from the members at the annual meeting, and hold office until the adjournment of the meeting at which their successors are elected.

The President, Vice President, Secretary and Treasurer shall be elected for one year, and the Trustees for three years; and no President, Vice President, or Trustee shall be eligible for immediate re-election to the same office.

The duties of all officers shall be such as usually appertain to their offices, or may be delegated to them by the Board of Trustees or the Society; and the Board of Trustees may at its discretion require bonds to be furnished by the Treasurer.

Vacancies in any office shall be filled by appointment by the Board of Trustees, but the new incumbent shall not thereby be rendered ineligible to re-election at the next annual meeting to the same office. On the failure of any officer to execute his duties within a reasonable time, the Board of Trustees, after duly warning such officer, may declare the office vacant, and appoint a new incumbent.

A majority of the Board of Trustees shall constitute a quorum; but the Board of Trustees shall be permitted to carry on such business as it may desire by letter.

ELECTIONS.

At the annual meeting, a nominating committee of five Members, not officers of the Society, shall be appointed, and this committee shall send the names of the nominees to the Secretary at least 60 days before the annual meeting, who shall immediately forward the same to the Members. Any other five members may also present the names of any candidates to the Secretary, provided it is done at least 30 days before the annual meeting. The names of all candidates, provided their assent has been obtained, shall be placed on the ballot without distinction as to nomination by the regular or an independent nominating committee, which shall be mailed to every member, not in arrears, at least 20 days before the annual meeting. The ballot shall be enclosed in an inner blank envelope, and the outer envelope shall be endorsed by the voter, and mailed to the Secretary for collection.

The blank envelopes shall be opened by three Scrutineers appointed by the Chair at the annual meeting, who will report the result of the election. A plurality of the votes cast shall elect.

MEETINGS.

The annual meetings shall take place on the first Monday in February, at such place as the Board of Trustees may decide, at which time reports shall be made by the Board of Trustees, Treasurer, and Scrutineers of election, and the accounts of the Treasurer audited by a committee of three appointed by the Chair.

Other meetings may be held at such times and places during the year as the Board of Trustees may decide, but at least 20 days' notice shall be given of such meetings.

Seven members shall constitute a quorum at any regular meeting, and a majority shall rule except when otherwise specified.

The order of business at the annual meeting shall be:

1. Reading of Minutes of last meeting.
2. Reports of the Board of Trustees and Treasurer of the Society.
3. Announcement of Election of Members.
4. Announcement of Election of Officers.
5. Appointment of Nominating Committee.
6. Old Business.
7. New Business.
8. Reading of Papers.

PUBLICATIONS.

The Board of Trustees shall act as a Publication Committee, and decide as to what to publish. The publications of the Society shall be sent to all Members and Associates not in arrears. The Secretary will furnish each author with reprints of his papers at cost price, provided due notice is given that reprints are desired.

The Society is not, as a body, responsible for the statements or opinions expressed in its publications.

PARLIAMENTARY STANDARD.

Roberts' "Rules of Order" shall be the parliamentary standard on all points not covered by these rules.

AMENDMENTS.

These rules may be amended at any regular meeting by a two-thirds vote of a letter ballot at the subsequent annual meeting, provided a written notice of such proposed change is sent to each member at least 30 days before said annual meeting. Said proposed amendments shall be printed on the ballot for officers and counted by the same Scrutineers.

PUBLICATIONS.

The publications of the Society are as follows:

	DESCRIPTION OF VOLUME.	Price to Members.	Price to Others.
Vol. I.	Transactions for 1899, 110 pages,		
	Bound in paper,	$0.50	$4.00
	Bound in cloth,	1.25	4.75
Vol. II.	Transactions for 1900, 278 pages,		
	Bound in paper,	2.00	4.00
	Bound in cloth,	2.75	4.75
Vol. III.	Transactions for 1901, 238 pages,		
	Bound in paper,	1.00	4.00
	Bound in cloth,	1.75	4.75
Vol. IV.	Transactions for 1902, 300 pages,		
	Bound in paper,	3.00	4.00
	Bound in cloth,	3.75	4.75
Vol. V.	Transactions for 1903, 420 pages,		
	Bound in paper,	3.50	5.00
	Bound in cloth,	4.25	5.75
Vol. VI.	Transactions for 1904, 278 pages,		
	Bound in paper,	2.50	4.00
	Bound in cloth,	3.25	4.75
Vol. VII.	Transactions for 1905, 454 pages,		
	Bound in paper,	3.25	4.50
	Bound in cloth,	4.00	5.25
Vol. VIII.	Transactions for 1906, 411 pages,		
	Bound in paper,	3.00	4.00
	Bound in cloth,	3.75	4.75
Vol. IX.	Transactions for 1907, 808 pages,		
	Bound in paper,	4.00	5.50
	Bound in cloth,	4.75	6.25
Vol. X.	Transactions for 1908, 582 pages,		
	Bound in paper,	3.75	5.00
	Bound in cloth,	4.25	5.50
The Collected Writings of Dr. Hermann August Seger, Volume I. Contains (A) Treatises of a general scientific nature. (B) Essays relating to Brick and Terra Cotta, Earthenware and Stoneware, and Refractory Wares. Pages 552. Bound in cloth,		7.50	7.50
The Collected Writings of Dr. Hermann August Seger, Volume II. (B) Essays on White Ware and Porcelain. (C) Travels, Letters and Polemics. (D) Uncompleted works, and extracts from the archives of the Royal Porcelain Factory. Pages 605. Bound in cloth,		7.50	7.50
A Bibliography of Clays and the Ceramic Arts, by Dr. John C. Branner, 1906, 451 pages. Bound in cloth. Contains 6027 titles of works on Ceramic subjects.		2.00	2.00
Cost of full set of Transactions, bound in paper,		$43.50	$61.00
Cost of full set, all bound in cloth,		$50.75	$68.25

At the Cincinnati meeting, the Board of Trustees fixed a sliding scale of prices to apply to the sale of volumes of the Transactions, when the number unsold falls below 200 copies. As the copies become scarcer, prices will be increased to both members and others. The supply of several of the volumes has already fallen below 200 copies, and others will probably pass below this mark during the coming year. Some of the volumes have already been raised in price for the second time. Members and Associates who do not yet own full sets are advised to procure them at once.

At the same meeting the following resolution was adopted:

Resolved, that the custom by which members and associates may obtain copies of the Transactions at reduced or so-called "members' rates," is intended only to enable each person to obtain one complete file of the transactions.

The necessity for this resolution arose from the expressed desire of a member to buy a copy of the transactions, with the intent to sell it to a friend for whom he wished to save the additional price charged to non-members. In accordance with the spirit of this resolution the Secretary will not supply more than one copy of a volume to a member at reduced rate, except when loss or destruction of a volume gives good cause for so doing.

Every member or associate receives one copy of the Transactions free for each year for which he pays dues. He is entitled to purchase copies for the years antedating his connection with the Society at the costs indicated in the first column. All others can obtain copies at the prices listed in the second column by sending order, accompanied with check, to

EDWARD ORTON JR., *Secretary.*

Columbus, Ohio.

IN MEMORIAM.

MAX SIMONIS, PH. D.

Dr. Max Simonis was born in St. Johann, Germany, July 27, 1882, and completed the course at the Royal Gymnasium, Saarbruecken. His university studies he pursued in Switzerland and at Freiburg, where he studied chemistry under Prof. Gattermann. After serving one year in the army, he returned to the University of Freiburg to complete his work, at the same time serving as lecture assistant to Prof. Willgerodt. On the basis of his thesis, dealing with an organic investigation, he was given the degree of Ph. D., cum laude.

During his vacation, Dr. Simonis was employed in the Saarbruecker Steel Works, and in 1904 he entered the technical experimental laboratory of the Royal Porcelain Manufactory, at Berlin, where his work soon attracted attention. His versatility, his sound knowledge of chemistry, physics and mathematics and his ability as an experimenter are clearly shown by his various publications on the use of the electric furnace for high temperature work with silicates, his entectic studies, his study of the viscosity of clay slips as influenced by various reagents, the work on the rearrangement of the Seger Cones, by which he eliminated serious errors, and others.

It was the hope of the American Ceramic Society, of which Dr. Simonis had recently became a member, that he would eventually become identified with American ceramics, but it was not to be. During a vacation trip to Italy, on climbing Monte Cinto, on the island of Corsica, he met with an accident on October 9th which caused his death.

The American Ceramic Society desires to express to the family and associates of Dr. Simonis, the sincere sorrow and sense of loss that they feel in the untimely end of this brilliant and able young scientist, who would surely have achieved still greater things for ceramics had his life been spared and allowed to come to its full fruition.

IN MEMORIAM.

PETER L. YOUNGREN.

Mr. P. L. Youngren was stricken with apoplexy while superintending the final test of one of his kilns at Summitville, Ind., on the 10th of August, and died a few hours later without regaining consciousness. His sudden death, in the prime of life, was a shock to his friends and acquaintances and to the brick manufacturers of America, to most of whom he was known by reputation, if not personally. He left a wife and seven children to mourn his untimely death.

Mr. Youngren was born in Sweden in 1862. Coming to America a young man he soon devoted himself to brick burning and to the development of a gas-fired continuous kiln adapted to conditions in this country. He found employment at various places from the Atlantic to the Pacific, settling in Milwaukee in 1891 upon his return from California. In Milwaukee he designed and constructed a gas-fired continuous kiln that overcame some of the troubles previously experienced in burning Milwaukee clays. This kiln, though improved upon considerably in after years, became the foundation of the kiln business by which he became known to all of us and by which he will be known for many years to come. His was no easy task. Even though continuous kilns are in universal use in Europe and even though the gas-fired continuous kiln had been successfully developed years before in Germany by Mendheim and others, yet American brick makers had become prejudiced against such kilns by the numerous failures here of incompetent foreigners, and were extremely cautious about making the large investment required. Moreover, the development of a new kiln under new and varied conditions must needs mean the running up against many unforeseen difficulties and consequently some failures or only partial successes. Mr. Youngren passed through these struggles enriched in experience, if not in purse. It is much to be regretted by his friends and by the Society that he was taken away just as his efforts were coming to be appreciated and his business established upon a profitable basis. It is indeed a pity that he could not have lived to reap the full reward of his labors.

The Society desires to record its appreciation of the character and services of its departed associate, Mr. Youngren, and to extend to his family its sympathy in their bereavment.

PAPERS AND DISCUSSIONS

ADDRESS OF THE RETIRING PRESIDENT.

ALBERT V. BLEININGER, Pittsburg, Pa.

Reviewing the work and growth of the Society during the past year, as evidenced in Volume X of the Transactions, I think we have reason to congratulate ourselves. We are not only prosperous from the material standpoint, as to numbers and finances, but we have gained in a far greater possession — the esteem in which this organization is held, both in America and Europe. Unique as it is in its aim and scope, held together by the bonds of friendship and good fellowship as few other technical organizations are, it occupies to-day the highest rank of any society devoted to the study of silicate technology in the world. Let us not, however, relax our efforts, but strive ever onward to the fulfillment of the important part that the Society is destined to play in the advancement of American civilization. There is much yet to do and we should be proud that it is our privilege to serve our country and our fellowmen in the field of ceramics, the importance of which is bound to grow as even the most optimistic of us cannot realize.

There are a few points pertaining to the policy of the Society to which I wish to call your attention.

Occasionally one hears the remark that it would be desirable to have all our papers written from the practical standpoint; that strictly scientific topics be eliminated. This is not a new subject and is one that is bound to come up from time to time. It has some justification, since in fact there is a decided shortage in strictly practical contributions, written from the factory standpoint. We ought to have many of such papers where now we have but few, and if there existed a tendency to crowd out the industrial side of our subjects by more or less ambitious attempts at scientific problems I would willingly

vote to exclude the latter. But such is not the case. There has been a constant plea for papers dealing with factory problems, such as could be written by every member engaged in the industrial side. We are in need of more practical papers by practical men and we must have them. There surely is no lack of subjects, as Prof. Binns has so ably pointed out in a former address, since every manufacturer constantly meets with problems the study of which would not only benefit himself but would be exceedingly interesting to us.

In this connection there might be suggested a closer cooperation between manufacturers and ceramic schools. I am quite positive that the latter would be glad to offer their assistance and advice to any member wishing to make a contribution but who might be in doubt as to the mode of attack, the apparatus required or similar questions. In this way workshop and laboratory would be brought together in the most satisfactory manner.

On the other hand also, we cannot do without the exact, logical contribution, supported by experimental evidence and dealing with the chemistry and physics of our operations. Scientific researches have played too great a part in the world's development to be disregarded. They contain the seed from which new ideas and applications spring. We ought to be proud to have scientific contributions developed within our own society; we need more of them, still more exact and more scientific. At the same time it should be our aim to express ourselves as clearly as possible. Frequently it is impossible to treat a subject with exactness in a popular way since it is difficult to find every-day equivalents for technical terms. Scientific language in its highest type is already as simple as exactness will permit, and we must be content with its nomenclature. However, the key-note should be — the constant aim for simplicity, both in treatment and language. There is no reason why the conclusions reached in each article should not be written in such plain and concise words that they may be understood by every man.

If a paper fails to do this I doubt whether it is worth a place in our transactions.

Let us be glad, therefore, that in our Society theory and practice are so happily blended. We should realize also that many of the strictly technical papers represent considerable financial outlay and personal sacrifice, not only in the work and preparation but also in the fact that by giving them to us they are withdrawn from the larger avenues of scientific intercourse and left in our own small lane. Thus they do not have the benefit of the large circulation that would be given them by the great scientific and technical journals of the world.

The writer is gratified indeed to realize that in the formation of a committee on the analysis of clays and clay testing during the past year an important step has been taken, perhaps more important than we realize. It will result not only in the collection and correlation of the data now existing as regards the examination of clays, but it will form the foundation upon which further progress will be built, so that we may hope that the future will finally bring order out of the present chaos.

I am glad to-day to resume my place in the ranks and enjoy the meeting with you more than has been possible in my elevated position as your presiding officer. I wish to thank you again for the honor done me and for your kind indulgence in my shortcomings and your cooperation in the fulfillment of my duties. I bespeak the same favor for my honored successor and hope that during his administration our Society may grow and prosper as it has in the past.

NOTES ON THE PRODUCTION OF CERAMIC RED COLORS.

BY

A. HEUBACH, Chicago, Ill.

It is safe to say, that of all colors used in the ceramic industries, the reds are those most difficult to produce. Not only is the composition of the color mixtures of importance, but also the use to which the colors are to be put must be considered. Further, the kinds of flux or glaze, as well as the temperature and the conditions of firing, are very essential for a good development of these colors.

There are different kinds of colors, classified according to the temperature at which they are to be fired, namely: enamel colors, colored glazes, underglaze colors for low and higher temperatures and colors for sharp fire.

For red enamel colors ferric oxide and gold are used. The ferric oxide has the peculiarity of changing its color from a light orange-red to deep cherry-red, according to the temperature to which it is exposed. The ceramist turns this peculiarity to advantage, heating the ferric oxide, produced by roasting sulphate of iron, as long and as high (temperatures up to the melting point of gold are permissible) as may be necessary to attain the shade desired. This is done best by drawing a trial every little while. When the desirable tint is reached, the firing must be discontinued. In this way the desired color is produced.

It is far more difficult, however, to find a suitable flux that enables the color to adhere to the ware without being changed. The experiments the writer made in this direction have not been extended far enough to allow an exhaust-

ive discussion in this paper. A flux, with which I obtained good results has the following formula:

$$1.0\ PbO \begin{cases} 0.5\ SiO_2 \\ 0.5\ B_2O_3 \end{cases}$$

Red brown to light brown enamel colors are produced by the use of chromium-iron, iron-alumina, and iron-zinc colors. For coral-red, Dr. Granger of the factory of Sévres recommends chromate of lead with a very basic flux. He gives the following formula:

Chromate of lead	28
Flux	75

The flux containing:

Minium	85
Flint	15

This color has a very high content of lead and is consequently very fusible and therefore has to be fired very carefully.

For the production of purple, carmine, and pink enamel colors, gold is used.

The opinions about the constitution of the gold-purples are as widely divergent as they are about that of the chromium-tin colors. Formerly gold-purple was supposed to have the formula $2Au+SnO_2$, but experiments made recently seem to show that it is a mixture of colloidal gold and colloidal stannic acid in different proportions.

For the production of gold-purple the well known reaction between gold chloride and stannous chloride is used, represented in the following equation:

$$2\,AuCl_3+3\,(SnCl_2+2H_2O)+3H_2O=(3H_2SnO_3+2\,Au)+12\,HCl.$$

From this equation it may be calculated how much stannous chloride is necessary in order to transform a certain quantity of gold into gold-purple, as the resulting precipitate contains all the gold used.

In industrial work stannous ammonium chloride is used instead of Stannous chloride, as this double-salt is not so easily decomposed in the aqueous solution into stannous hydroxide and hydrochloric acid as stannous chloride would be.

The above equation would then appear as follows: $2\ AuCl_3+3(SnCl_2 2NH_4Cl+2H_2O)+3H^2O=(3H^2SnO_3+2\ Au)+6NH_4Cl+12HCl$.

Stannous ammonium chloride is produced by pouring together the boiling concentrated solutions of 68 parts of stannous chloride and 32 parts of chloride of ammonium.

The different shades of purple colors are obtained by adding corresponding quantities of stannic ammonium chloride, $Sn\ Cl_4 2NH_4Cl$ (pink salt). The different shades result from the distribution of the gold purple, shown in the above equation, upon the hydroxide or oxide of tin, introduced into the solution by adding the pink salt. Consequently the tint of the color is the lighter the more pink salt, i. e. oxide of tin, is used.

Ammonia alum, $Al(NH_4)\ (SO_4)_2+12H_2O$, is used for the production of pink colors, instead of the pink salt, that is, the alumina takes the place of the oxide of tin.

It is necessary, however, in order to obtain good results that the solution of the gold chloride be diluted with water to a great extent, — about 4 gallons to 1 gramme of metallic gold.

The solution of the pink salt is first to be poured into the solution of the gold chloride and afterwards with constant stirring the solution of stannous chloride, corresponding to the quantity of gold, must be added carefully.

The precipitation of the alumina-purple is similar, but finally a little ammonia must be added in order to precipitate the alumina. The precipitate is flocculent and of a dark violet-brown color. It settles more rapidly and better if a few drops of sulphuric acid are used.

This precipitate should be washed carefully by decan-

tation until nitrate of silver solution does not give any further reaction.

The purple thus obtained is preserved best in wet condition. After it has been washed sufficiently, the supernatant liquid must be decanted as far as possible and then the precipitate, together with the rest of the liquid, is poured into a graduated cylinder and diluted up to the mark by addition of pure water.

From the quantities of the materials used there may be calculated how much stannic acid — oxide of tin — and how much gold — gold-purple — this quantity of liquid contains.

In order to prepare the color for use, the graduate and contents are thoroughly shaken, and a definite quantity of the mixture is removed by means of a pipette and mixed with the flux.

The different purples are distinguished by their content of gold relative to 100 parts of tin oxide.

The writer found as good fluxes those of the following formulae:

$$\left.\begin{matrix} 0.75\ PbO \\ 0.25\ Na_2O \end{matrix}\right\} \begin{matrix} 0.5\ SiO_2 \\ 0.5\ B_2O_3 \end{matrix} \quad \text{and} \quad \left.\begin{matrix} 0.65\ PbO \\ 0.12\ K_2O \\ 0.23\ Na_2O \end{matrix}\right\} \begin{matrix} 0.75\ SiO_2 \\ 0.50\ B_2O_3 \end{matrix}$$

and for pink colors — alumina-purples —

$$\left.\begin{matrix} 0.8\ PbO \\ 0.2\ Na_2O \end{matrix}\right\} \begin{matrix} 1.00\ SiO_2 \\ 0.40\ B_2O_3 \end{matrix} \quad \text{and} \quad 1.00\ PbO \quad 1.00\ B_2O_3$$

Brongniart gives the following fluxes:

$$\left.\begin{matrix} 0.85\ Na_2O \\ 0.15\ PbO \end{matrix}\right\} \begin{matrix} 1.70\ SiO_2 \\ 1.66\ B_2O_3 \end{matrix} \quad \text{for carmine.}$$

$$1.00\ PbO \left\{\begin{matrix} 0.79\ SiO_2 \\ 1.90\ B_2O_3 \end{matrix}\right. \quad \text{for purple.}$$

$$1.00\ PbO \left\{\begin{matrix} 0.28\ SiO_2 \\ 0.74\ B_2O_3 \end{matrix}\right. \quad \text{for violet.}$$

It is necessary, however, to add a small percentage of carbonate or chloride of silver in order to produce carmine and purple colors. Without silver they all turn violet,

but if too much silver is added the colors show a yellowish tint.

All colors mentioned above must be fired in a strictly oxidizing atmosphere and at a low temperature (about 800°C.). Especially the iron colors are completely destroyed if the temperature rises too high.

These colors may be used on glass and all glazed products of the ceramic industries. They are mixed with some kind of resinous oil and applied to the ware by means of a brush or an air brush.

For higher temperatures the well-known chromium-tin colors are used either as underglaze colors or as coloring ingredients in glazes. These colors are used in the majolica, terra-cotta, faience, earthenware and stoneware industries. Seger even used them successfully at cone 9 as underglaze colors on the chinaware named after him. Beyond this temperature, however, they will hardly show good tints.

So many divergent reports about the production of the chromium-tin colors have been published that it seems unnecessary to discuss the matter in this paper. I found the following as serving the purpose:

dark red:	0.0047 K_2O 0.9768 CaO 0.0184 PbO	0.011 Cr_2O_3	1.11 SiO_2 1.12 SnO_2 0.005 B_2O_3
pink:	0.013 K_2O 0.987 CaO	0.013 Cr_2O_3	2.26 SiO_2 1.31 SnO_2
lilac:	0.45 K_2O 0.55 Na_2O	0.45 Cr_2O_3	14.28 SnO_2 1.10 B_2O_3

The two first mentioned colors turn out the best if fritted at about the melting point of silver and, after careful washing, burned at cone 4. It is, however, sufficient for the lilac color to frit it at a temperature between the melting point of silver and that of gold.

After extensive experiments I came to the conclusion that for the production of red glazes the composition of the colors is not so essential as that of the glazes that are to develop the colors.

About this subject, also, many articles have been published, but the opinions are widely divergent. The writer obtained good results, which will stand comparison with the best English chromium-tin glazes, by using glazes which contain lead to a great extent and none or only little boric acid. It is impossible, however, to give a glaze formula that will be suitable for the firing conditions of the different factories, rather each factory must find out the glaze most suitable for its purposes. I obtained, for instance, beautiful results in a muffle kiln fired 120 hours, while the same glazes fired under the same conditions in a trial muffle for a period of 10—12 hours only, turned to a grayish-green tint, showing not even a trace of red.

If the chromium-tin colors are to be used as underglaze colors, they must be mixed either with kaolin, or the body-mixture or glaze, first in order to make them adhere better on the body and then in order to make them unite with the glaze more easily. The most suitable proportions between the above-mentioned materials and the colors, must be tried out in every case.

Before discussing the colors for sharp fire I will give a few hints as to the production of those red copper glazes, generally known as *Rouge flambé, Sang de bocuf* and so on.

Such glazes develop best between cone 4 and cone 7. The most important condition, in order to obtain good results, is that of firing. The glazes must be fired in a reducing atmosphere. They turn brown, however, mingled with spots of a metallic appearance, if they are reduced too much. In order to avoid this, Seger suggests to fire from time to time with an oxidizing flame for a few minutes. After the glaze shows a glassy appearance it may be fired oxidizing to the end.

There is not much to be said about the composition of these glazes. They must be fusible, rich in alkalies and must contain but a little copper oxide. Seger obtained good results with 0.10 to 0.15% for dark red tints and 0.5 to 1.0% for lighter tints.

While Seger's formulae for red copper glazes contain barium oxide, I obtained good results with the following glazes:

0.30 CaO 0.07 MgO 0.16 K_2O 0.29 PbO 0.12 Na_2O 0.06 CuO	0.20 Al_2O_3	1.06 SiO_2 0.11 B_2O_3 0.07 SnO_2	for a bluish red.
0.25 CaO 0.05 MgO 0.14 K_2O 0.32 PbO 0.12 Na_2O 0.05 ZnO 0.07 CuO	0.18 Al_2O_3	2.40 SiO_2 0.12 B_2O_3 0.05 SnO_2	for a nice blood red.
0.31 CaO 0.02 MgO 0.10 K_2O 0.22 PbO 0.11 Na_2O 0.13 ZnO 0.09 CuO	0.20 Al_2O_3	1.75 SiO_2 0.22 B_2O_3 0.09 SnO_2	for a light red

These glazes developed best between cone 5 and cone 7. It may be seen from above formula that all three glazes contain a considerable amount of lead. Compared with those given by Seger and other authors, great differences as to their composition may be observed. This fact proves the statement, that good results depend more on the firing conditions than on the composition of the glaze. Besides, my experiments confirm Seger's statement, that dark colors result from a small content of copper, while the colors turn lighter corresponding to the increasing amount of that metal. Seger explains this fact as follows: In glazes with a small content of copper, the resulting cuprous oxide is completely dissolved by the glaze. Consequently the glaze turns out transparent and makes the color appear darker and more beautiful, while a greater amount of copper renders the glaze opaque and lighter tinted.

Copper-red glazes may also be produced by reducing the surface of the glaze only. For this purpose the glazes

are fired in a muffle in an oxidizing or neutral atmosphere and after they have fused, either oil, or sawdust, or other materials that produce reducing gases are put into the muffle and the air completely shut out.

After Seger and Zolnay's experiments the Royal Doulton factory at London experimented and now produces such glazes successfully.

For red sharp fire colors, i. e., for colors fired at a higher temperature than cone 9, only gold and chromium-aluminium colors can be used, as all other colors are destroyed at a temperature as high as that. These colors can only be used as underglaze colors, or as coloring ingredients for the body mixture, while red glazes are altogether unknown for these temperatures. I tried a chromium-alumina color in a matt glaze, but the glaze turned green, appearing red only when exposed to artificial light. *Professor Petrik reports a similar experience.

The gold colors may be produced in different ways. For the production of liquid colors, i. e., color-solutions, the gold chloride is dissolved in concentrated glycerine. In order to avoid an overflowing of the colors beyond the outline of the drawing, a more or less concentrated solution of dextrine or sugar is added. The intensity of the colors depends on the amount of gold dissolved. The glycerine solution is of an orange-yellow color. If dextrine is added, the gold chloride is reduced and the gold settles after some time as a dark violet-brown precipitate exceedingly finely divided, similar to the gold purple mentioned above. In such case the solution must be shaken thoroughly before using.

For substantial underglaze colors the aqueous gold chloride solution is added to a definite quantity of body slips, or kaolin suspended in water, the quantity according to the tint desired. After stirring thoroughly the gold is precipitated directly in the slip by means of sodium hydroxide and glycerine or grape sugar, or stannous chloride.

*Sprechsaal No. 27, 1907.

The color thus produced is lightly roasted, after thorough washing, and is then ready for use.

Colored slips are produced in the same way.

The colors just mentioned may also be used as sharpfire colors upon the glaze. The writer obtained good results by precipitating the gold in kaolin slip and roasting the mixture. It is sufficient, however, simply to dry the kaolin slip with the gold-solution and afterward to roast it. I added 75 to 100% of a glaze to the color thus prepared and applied the final mixture to the ware in the same way as it is done with the enamel colors. It is logical, of course, to use the same glaze upon which the color is to be applied afterward. In this way I obtained a very nice pink color at cone 14.

As mentioned above only chromium-alumina colors may be used besides gold. The chromium-alumina colors serve the same purposes as the gold colors, but show tints different from those of the gold colors. Their composition is similar to that of the chromium-tin colors, but alumina takes the place of tin oxide. As a coloring ingredient for bisquit ware, I used successfully a color of the formula:

$$1.0\,K_2O \left\{ \begin{matrix} 16.53\ Al_2O_3 \\ 1.00\ Cr_2O_3 \end{matrix} \right\} 3.27 B_2O_3$$

After firing the color to about cone 14, it should be washed carefully. When added to the body mixture it furnished a nice violet-red, that appeared intensely blood-red when exposed to artificial light.

While this color cannot be used as underglaze color, I obtained a beautiful salmon color by using the following formula as an underglaze color:

$$\left.\begin{matrix} 0.046\ K_2O \\ 0.658\ MgO \\ 0.296\ ZnO \end{matrix}\right\} \left\{ \begin{matrix} 0.722\ Al_2O_3 \\ 0.046\ Cr_2O_3 \end{matrix} \right\} 0.08\ B_2O_3$$

This color is treated in the same way as the previous one. If mixed with 30—40% of body mixture or kaolin the color is ready for use.

Dr. Granger gives a chrome-aluminate of the following formula:

Alumina	100.0
Bichromate of Potash	7.5

*Professor Petrik gives a color containing:

Ammonia Alum	882
Bichromate of Potash	10

He also gives another containing zinc, as follows:

Aluminium hydroxide	83.0
Zinc sulphate	35.5
Bichromate of Potash	10.0

All chromium-alumina colors must be fired, if possible, higher than the ware on which they are to be applied.

They show nice tints at the highest temperatures used in the ceramic industries.

DISCUSSION.

Mr. Burt: I would like to ask what temperature is referred to in speaking of high temperature in firing the chromium-aluminium reds?

Mr. Hottinger: It refers to a porcelain fire, which varies in Europe from cone 10 to cone 16.

Mr. Stover: Under our regular lead glaze chrome-tin pinks would vanish at anything above cone 8 or 9.

Mr. Burt: Is that correct?

Mr. Stover: Yes, sir. The reason I know is that I put through quite a large series of trials to disprove that point, seven or eight years ago, and I found by calcining the oxide of tin and bichromate of potash, and burning in a reducing atmosphere, we could go considerably above cone 10, and by using a raw glaze high in lime I was able to get a pink, as we call it, higher than that. I made thirty or forty different shades of what we call chrome-tin pink above cone 10.

*Sprechsaal No. 27, 1907.

Mr. Binns: Do I understand that was a reducing atmosphere?

Mr. Stover: Yes. I fired it in little round balls or marbles so the fire gases could get to it. Some old receipts called for firing in open saucers. In open saggers on the bags I got a better pink than in the saucer.

Mr. Binns: That is perfectly true, because you got more oxygen.

Mr. Purdy: Were you referring to the stain there?

Mr. Stover: Yes, sir; the stain.

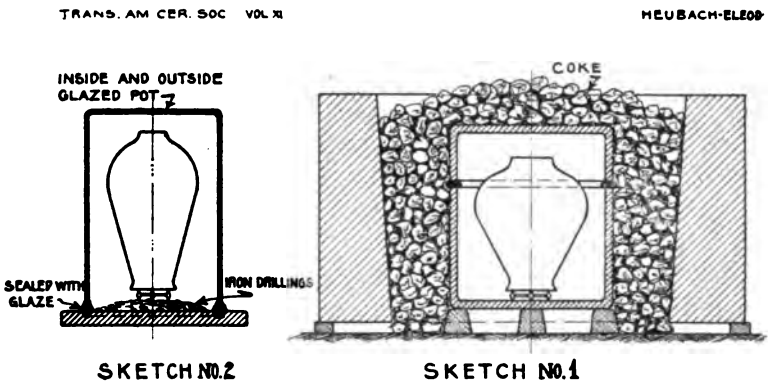
Mr. Jackson: I think to any one working in gold solutions this paper by Mr. Heubach would be very valuable; and for my part I am very glad to see the data given for publication in our transactions.

Mr. Ashley: Mr. President, at last year's meeting, Mr. Worcester presented a paper on crystalline glazes, in which he mentioned some work in the use of Ceramic Iron-free Rutile of the Foote Mineral Company and their Standard Ruby Rutile. He was unable to detect any difference in the use of those two rutiles. I happened also to receive samples of those rutiles two years ago and tried them mixed with a glaze quite near the ordinary earthenware glaze in composition. In one case I used ten parts of the Ceramic Iron-free Rutile to ninety parts of the glaze, and in another used the same proportions with Standard Ruby Rutile. I noticed no great difference. Both were a straw-yellow. The Iron-free Rutile, in a proportion of five per cent, produced merely a paler yellow color. If the ruby rutile was reduced to five per cent, a ruby color came out very plainly. By decreasing the proportions further, the color gradually faded out entirely. These were fired to cone 6 in an oxidizing atmosphere. It is rather interesting as a possible source of ruby colors. These trials were made by merely mixing the sample with the glaze in a mortar, and no precautions were taken for thorough grinding and mixing. I will leave them here so they may be available if any one wants to examine them.

Mr. Binns: Mr. President, I will ask Mr. Ashley to what he attributes the ruby color there?

Mr. Ashley: I have no theory whatever.

Mr. Elcod: Some time ago, experimenting with *Rouge flambé*, — I followed Seger's instructions in the matter closely and secured very nice specimens of copper reds— all kinds, under the glaze, on the glaze and in the glaze. Since Seger laid down the theory of how to maintain copper oxydul (Cu_2O) in silicates (*Sang de boeuf or Rouge flambé*), he made it possible for us to duplicate more accurately these effects, which originated with the Chinese and Japanese.



I fired them in coke ovens, in saggers (No. 1 sketch), also in ordinary kilns, in clay boxes (No. 2 sketch), in which a certain quantity of iron drillings (according to the size of the boxes) acted as a reducing agent resp. oxidizing.

These ways, the results are very uncertain, being entirely out of one's control.

But *Rouge flambé* can be manufactured and it is manufactured commercially. For that, a kiln is used, in which the reducing resp. the oxidizing atmospheric conditions can be easily changed at short notice.

METHOD FOR MEASURING VOLUME OF SEALED PORES.

BY

ROSS C. PURDY, Columbus, Ohio.

The validity of the expression $\left(\frac{T-A}{T}\right)100$ as expressing the percentage volume of the sealed cavities has been challenged. The challenger showed by calculations that these cavities might be filled with a highly attenuated gas approximating a vacuum. Because these cavities are practically vacua, he inferred that weighing the test pieces in air results in false readings. Since the weight of air is $\frac{1}{773}$ that of water, he concludes that even if filled with air, these cavities would buoy up the piece in the water and hence give false suspended-weight readings.

Granting that these cavities may be filled with a very highly attenuated gas, it remains that the error introduced in calculations based on the above formula is considerably smaller than the usual experimental errors met with in such determinations. If these cavities were filled with air at the same temperature and pressure as the air surrounding the test piece at the time of weighing, the above formula would be correct, as it stands. If the cavities are virtually vacua, corrections must be made to the weight of the test piece for the buoyancy of the air, if extreme accuracy is demanded.

The weight of a body in air is less than its real weight by the weight of the air it displaces. This is the principle of Archimedes, holding just as true in air as in water. This same principle is as true for the counterbalancing weights as for the body which is weighed. Since this applies to both, a correction made for the buoyancy of air must involve both, and must be dependent upon their relative densities.

Let x stand for real mass of the body in grams.
Let w stand for real mass of the weights in grams.
Let D stand for the density of the body.
Let d stand for the density of the weights.
Let a stand for the density of the air.

Now since weight÷density=volume, the volume of the body will be $\frac{x}{D}$ and of the counterbalancing weights $\frac{w}{d}$. Then $\frac{x}{D}$ a and $\frac{w}{d}$ a respectively are the masses of air displaced by the body and the weights.

Archimedes' principle states that when a body is immersed either partly or wholly in a fluid, it displaces a volume of the fluid equal to the volume of the immersed part, and it is subjected to an upward force, due to the fluid, equal in magnitude to the *weight* of the volume of fluid displaced. This upward force to which the immersed piece is subjected, results in an apparent loss in weight. The weight of a body in air, therefore, must be less than would be the corresponding weight in a vacuum.

Algebraically, the weight in air for the body and counter-balancing weights respectively would be:

$$x - \frac{a}{D}x \text{ and } w - \frac{a}{d}w.$$

Since the weight of the body and of the weights counterbalance in the air, these two expressions can be equated thus:

$$x - \frac{a}{D}x = w - \frac{a}{d}w, \text{ from which by reduction}$$

$$x = w\left(1 + a\left(\frac{1}{D} - \frac{1}{d}\right)\right) \text{ nearly}^1.$$

The density of air (a) under normal conditions, is 0.001294 or, more exactly $\frac{1}{773}$. If brass weights are used (d) will equal 8.4.

[1]The exact value for x is $w\left(1+a\left[\frac{1}{D}-\frac{1}{d}+\left[\frac{a}{D}-\frac{a}{d}\right]\frac{1}{D-a}\right]\right)$

Applying this correction for the specific gravity (which is the weight of the piece reduced to basis of a unit volume) in an example given by Watts.(1) We have for the true specific gravity (x):

$$x = 2.3\left(1 + \frac{1}{773}\left[\frac{1}{2.3} - \frac{1}{8.4}\right]\right)$$

$$= 2.3(1+0.0004)$$

$$= 2.3009$$

For the apparent specific gravity:

$$x = 1.94\left(1 + \frac{1}{773}\left[\frac{1}{1.94} - \frac{1}{8.4}\right]\right)$$

$$= 1.94(1+0.0005)$$

$$= 1.941$$

The percentage volume of the sealed pores calculating that they are vacua, amounts to

$$\left[\frac{2.301 - 1.94'}{2.301}\right] 100 = 15.645$$

The percentage volume without the correction factor was 15.65. This proves that no appreciable error is made when the sealed cavities are considered as being filled with air instead of a highly attenuated gas as suggested.

In regard to these sealed cavities filled with air or gas buoying up the piece, there ought to be no room for argument. The presence of the cavities *does* result in a buoyancy that is directly proportional to the volume of the cavities and the density of the surrounding medium. This consideration was used in the above calculations.

Although it was not clearly stated, I infer that the challenger claims that because of this buoyancy an error is made in my calculations by not considering these cavities as filled with water, i. e., "having a density of 1."

(1) Vol. X, p.——

I have shown that for our purposes, it makes no difference whether the cavities are empty or filled with air. It ought to be obvious also that this very buoyancy *is the volume measure of the air-filled or vacuum cavities.* It certainly should be obvious that a solid equal in volume to the cavities would be buoyed up to the same extent. Buoyancy, according to Archimedes' principle, is due to and measured by the amount of water displaced. The fact that one body will float and another of the same volume sink, must not be taken as indicating a difference in the buoying force exerted in each case by the water. In one case the buoying power of water is greater than gravity and in the other, less. Amount or extent of buoyancy is not affected by the density of the buoyed object.

In my formula, the apparent density is a composite density of the solid material and of the gaseous (?) material in the cavities. The true density is the density of the solid material taken alone.

I have proven that my formula is correct and that it makes no difference with what gas, if any, the cavities may be filled. When the volumes of the cavities as calculated on this formula, is obviously too large, the data on which the calculations are based must be wrong.

Another and perhaps a more rigorously accurate, as well as more simple reduction of specific gravity from air to vacuum basis, is as follows:

In the expression for specific gravity ($\frac{D}{D-S}$), D, the weight of the piece in air, is subject to reduction to vacuum while S, the weight of the piece when suspended in water, however, is equal to the D—S, is not subject to reduction weight of water displaced. This weight of water displaced is subject to reduction. If W be the weight of water displaced, the formula for specific gravity becomes on reduction:

Sp. Gr. (V)= $\frac{D+\frac{a}{W}W}{W+\frac{a}{W}W}$ where a is the density of air. Dividing both the numerator and denominator thru by W we

have

$$\text{Sp. Gr. (V)} = \frac{\frac{D}{W}+a}{1+a} \text{ or } \frac{Sp.+a}{1+a}$$

Hence,

$$\text{Sp. Gr. (V)} = Sp. + a - a\,Sp - a^2$$

Since a^2, $\left[\left(\frac{1}{773}\right)^2\right]$ is very small, it may be neglected and our formula for Specific Gravity in vacuo becomes

$$\text{Sp. Gr. (V)} = Sp. - a\,(Sp. - 1 \text{ or } Sp. - \left(\tfrac{Sp.-1}{773}\right))$$

Specific gravity reduced to vacuum basis by this method is less than that on the "air basis" while by the other method it is greater. This discrepancy is due to the fact that in one case we reduce the weight of water to vacuum basis, ignoring the reduction of the counterbalancing weights, and in the other, the counterbalancing weights are reduced and the water ignored. The counterbalancing weights being denser than the object causes, on reduction, an increase in the specific gravity, and the water being less dense, causes a decrease.

If both the counterbalancing weights and the water, should be considered in the reduction formula, it is obvious that (theoretically as well as practically) hardly any correction would be made to the specific gravity of claywares as ordinarily determined.

NOTE ON DISINTEGRATION BY CRYSTALLIZATION AND FREEZING.

BY

JOHN W. COBB, Leeds, England.

In a careful and detailed study termed "The Relation of Hardness of Brick to their Resistance to Frosts," by J. C. Jones, (*Trans. Am. Cer. Soc.* Vol. IX, p. 528), the author discusses with special attention the nature of the physical action by which the freezing of water effects the disintegration of bricks. There is no need to emphasize the importance of such a study. I should like to point out, however, that the assumption seems to be made rather too readily, that the expansion of water is the primary force at work, and that the force of crystallization of water into ice, irrespective of expansion, is too lightly regarded. Some time ago, while working out, in the laboratory of the Farnley Iron Co., simple methods for the testing of glazed clay ware (v. *Journ. Soc. Chem. Ind.*, 1907, p. 28), I was led, on the score of convenience, to use the repeated crystallization of a cooling saturated solution of sodium thio-sulphate (photographers' "hypo"), instead of the freezing of water, as a test for the soundness of structure of a brick, and the firm adhesion of the glaze. In making the test the brick was dipped in a warm saturated solution of hypo, and allowed to cool; crystallization of the salt followed, and the process was repeated as often as necessary, until partial destruction of the brick or glaze resulted. (See Figs. 1 and 2). The fact of disintegration was expected, but the degree and rapidity of the effect realised were to me surprising. It seemed that the action of water in freezing was duplicated in the crystallization of the hypo, qualitatively, and so far as could be judged from the crude com-

parison possible, quanitatively also. If then the action of water in freezing was due to its expansion, was not expansion to be looked for in the crystallization of the hypo? This was made the subject of experiment by Dr. Dawson at the Leeds University laboratory and he found that no expansion but a positive contraction accompanied the crystallization.

FIG. 1.

It was so made plain that the disintegrating force at work when crystals of hypo formed in the porous solid such as a brick, was not the simple force of expansion, but must be another force associated with the crystallizing of the salt, more complex in character, which we may call

for convenience the "force of crystallization." It also seems natural to conclude that in all probability when water freezes (or crystallizes) its "force of crystallization" is sufficient to account for its disintegrating action, without attributing anything to the force of expansion. In saying this, there is no disposition to state that the effects of dis-

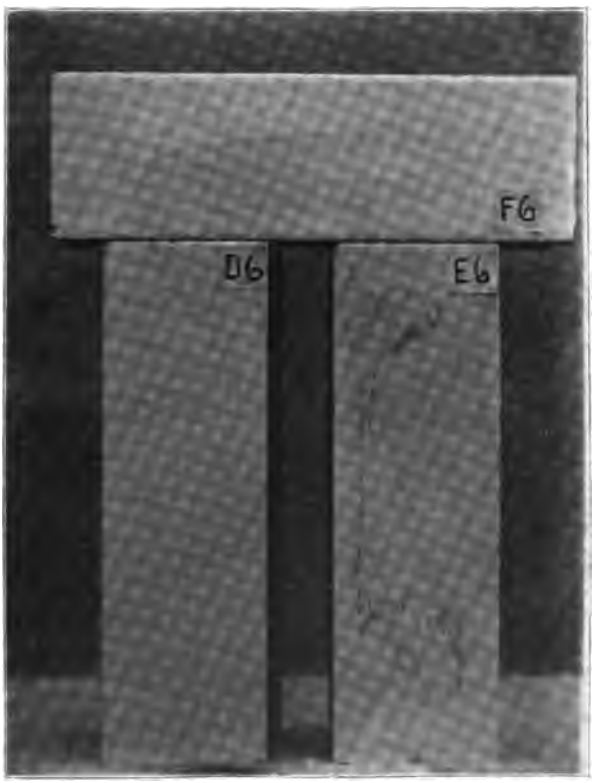


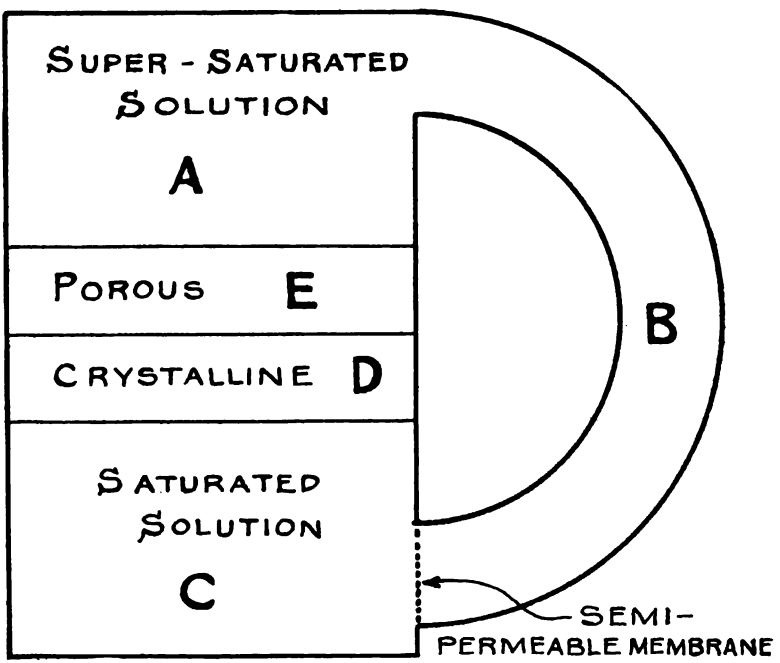
FIG. 2.

integration which have by long tradition been attributed to expansion are not due to this cause, but only the desire to point out that there is another force at work which is quite capable of doing all that is at present attributed to the assumedly dominant force of expansion.

Mr. Jones mentions the force of crystallization and refers to work done upon it, but in this connection it seems to me does not give it sufficient consideration.

The wide-spread geological phenomenon of the disintegration of rocks is bound up with the same question, for such disintegration may not be due primarily to the force of expansion of water in freezing, but to the "force of crystallization of water" into ice.

TRANS. AM. CER. SOC. VOL. XI. COBB.



To explain the nature of this force of crystallization — to show physical understanding of it by measuring its value is no easy task. The phenomena of surface tension have made us familiar with the strange forces which are called into play by the energy residing at the separating

surface of two media. Dr. H. C. Pocklington, F. R. S., in a letter to me, suggests the following explanation:

"The thick line represents an impervious substance (see sketch). If all the temperatures are the same the system reaches a state of equilibrium and the pressures in A and B are equal. That in C is greater by the difference of osmotic pressure of the liquid in B and C. Therefore, there is a pressure between D and E equal to this difference, and this is the pressure that the crystal can give rise to in its formation. We disregard gravity or put everything horizontal."

The nature of the results suggest the existence of a force which, by tending to secure continuity in the crystal-form enables the growing crystal to displace adjacent matter, and so to exercise a disruptive action on any material enclosing it, and in a study of disintegration by freezing, this force seems to call for full recognition.

DISCUSSION.

Mr. Bleininger: I would say that this kind of a test was applied some years ago, by Prof. Bauschinger of Germany, and an account of it was published as early as 1860. This crystallization of the salts of clay is an important question. It was impressed upon me recently by a pretty illustration which I noted in a German periodical. The roofing tiles made in a certain German town were frequently giving trouble owing to the disintegration of the top of the tile, and a careful investigation was made as to the cause. The tiles were taken and tested for crushing strength and porosity and also tested for freezing. The person making the test was surprised to find the porosity was not excessive, nor was the crushing strength defective, so, finally, in order to clear up this difficulty, he had the tile analyzed — the bottom part of the tile and the top part. In this way he found the true explanation. It was found that although the average portion of the tile was only about 0.2 per cent SO_3, in the top of the tile it was

6 per cent — more than thirty times as much was found in the top. By capillarity and the absorption of the rain the salts moved upward. The salts crystallized and the parts flaked off.

Mr. Richardson: I noticed a few days ago in the last report of the American Society for Testing Materials a paper by an official (J. Y. Jewett) of the United States Reclamation Service, upon the disintegration of concrete by the alkali waters of the West. He described the effect seen in the disintegration of pipe culverts which are partially submerged in the small streams carrying the drainage of the surrounding country. The disintegrating effect was more particularly noticed in the breaking up of the structure at the line where the water rises and falls, where there is a submersion followed by a drying out, followed by another submersion, etc. This process brings about a breaking up of the structure, similar in appearance to that of the effect of freezing, only much more severe. The engineer in charge of this work described the effect as follows:

"Have examined pieces of these culverts taken from below water level and found, by microscopic examination, minute crystals which disintegrate to a fine powder on being exposed to the air. This process of crystallization has an enormous expansive force, the same as freezing, and this undoubtedly has an enormous disintegrating effect. One culvert which had been in alkali water several months had no strength at all and was like so much sand and mud at the water level."

In studying the cause of this disintegration an analysis of the water gave the following composition:

	mg. per l.
$CaSO_4$	1,690
$MgSO_4$	6,870
MgH_2CO_2	305
$MgCl_2$	192
KCl	20
Total Solids	9,077
Loss on ignition	222

The principal mineral ingredient being magnesium sulphate, Mr. Jewett concludes that the effect of this water in causing disintegration of concrete is similar in its action to that of sea water, in which magnesium sulphate is believed to be the chief cause in producing disintegration of concrete structures in the sea.

Mr. Langenbeck: The paper is of great interest and I dislike to divert the discussion to a merely practical application. However, it has become very important to find a ready laboratory test that can be applied to ceramic products like tile and terra cotta which will demonstrate if the ware is capable of standing exposure to the weather without being destroyed by frost. Artificial freezing tests are cumbersome and expensive to make and they are not always positive in their results. This paper points to the possibility of using crystallizing salts as a substitute for freezing water for such tests and they may be more positive in their action as they are certainly much easier to apply in the laboratory.

Where wares are homogeneous in structure, even though they are not burnt to the hardness of steel, they resist the action of frost satisfactorily. But if the body of the ware is porous and it is covered with a mere vitreous skim the ice crystals do not exude freely on freezing, the ware goes to pieces after repeated frosts. This is the case with the red tile known as Welsh Quarries now used largely in this country. Exposed in outside terraces they do not withstand our climate but go to pieces for the reason stated.

This fact is true even in greater degree with glazed or semi-glazed porous terra cotta and tile which are to be used for the exterior decoration of buildings. The glaze covering is insufficient to prevent water from getting into the body of the ware or at least into some pieces of it, and in the course of time these pieces then break out after repeated frosts.

I have been told by terra cotta manufacturers in an off-hand way that in accordance with their experiences

such glazed ware is safe if the porosity is reduced to a water absorption of 6%. I want to ask the terra cotta manufacturers and the paving brick manufacturers if they have any particular experience proving that this figure is a safe one. If there is no positive information on this, laboratory tests by means of crystallizing salts as indicated in this paper may give very valuable data.

Mr. Gates: In this matter our tests have been somewhat like the tests of the common building brick made in Chicago. They built walls one story, then two, then three, four, six, eight and sixteen and they stood, but the test was not figured from an engineering crushing strength, but by practical trial, and this has been the case with terra cotta. The ware has stood, and I have known of no case in which properly made terra cotta has perished or failed. My opinion is that the very fact of the vitreous surface, impervious as it is, prevents the accumulation of the soluble salts beneath it. Suppose the whole mass back of the vitreous surface is porous and becomes saturated with moisture, as it would become when first placed, from the moisture of the mortar or cement backing for instance, then the soluble salts are dissolved in the water and transported by it wherever it goes. This water cannot pass through the vitreous coating and be evaporated and thus continue to deposit the salts there, but its only escape is in fact, back from the coating and away from it and into the back wall, and to an extent out through the joints, so that it will carry and deposit these salts away and really free the surface under the glaze or vitreous slip from the salts originally there, instead of increasing the content there. This is my theory only, but the practical results of twenty and more years bear it out in our terra cotta and also in large vases which have stood out doors for ten or twelve years.

In Egypt I noticed the disintegration of the rock in the old buildings where there is no action of frost. In many cases the bases of these ruins are subject to the overflow of the Nile, and could readily see where the rock was

much disintegrated where the overflow occurred about the bases, and at the dirt surface, and I concluded that the soluble salts were brought up from the soil and deposited there by capillarity and evaporation, and that the disintegration was brought out wholly by the force of crystallization.

We have had going recently in our laboratory, quite a line of experiments as to shrinkage in connection with porosity, but I haven't it sufficiently in mind to give any interesting data.

Mr. Langenbeck: Would you say six percent absorption was a high or low porosity on glazed ware?

Mr. Gates: I should think it was rather a high porosity.

Mr. Langenbeck: Your impresion is, a semi-glazed ware, which must stand outside exposure ought not to have or go over six per cent, laying down that as a broad rule for water absorption. Would it be a safe maximum?

Mr. Gates: That would be my offhand impression.

Mr. Lovejoy: The impression I got from the paper was, that there is contraction in the process of crystallization considered from the standpoint of an individual crystal, but as the crystal grows, it exerts a force due to its growth.

Crystals may interlace leaving pore spaces, and while the crystals may have greater density indicating contraction, the mass volume is greater.

A crystal may grow and force apart the walls within which it is confined, yet not completely fill the space in which it grew.

If the walls are sufficiently resisting, the crystal becomes deformed and in its growth is forced to follow the walls within which it is confined.

It seems to me it is more a question of the size of the pores rather than the degree of porosity. Now, while a brick may be very porous there are not necessarily any large spaces. A brick may be more porous when made of dry clay, than when made of stiff mud, but the pore spaces

are smaller. I found very soft burned dry pressed brick would stand the winter exposure, but the same material made into a stiff-mud brick and soft burned would go to pieces in one winter. I have attributed it to the fact that the voids in the stiff-mud product were larger and the water contained therein, in freezing exerted greater force and would cause flaking, while in the dry-pressed bodies, the smaller pores do not permit the accumulated force of greater volume and the porous face accompanying them, allowed the water to squeeze out. I recall two different rocks we had in Southern Ohio, one was a flinty limestone, very hard, and almost impervious to water in sample pieces. We also had a very soft sandstone, so soft you could cut it with a hatchet. The sandstone was a good building material as far as the frost resisting qualities were concerned, but the flinty rock was impossible, — it would go to pieces the first season, simply because the water that got into the cracks in the limestone gave a sufficient volume to break the stone asunder, while the softer sandstone, with its greater porosity and taking a larger amount of water, yet because of the small pores, the water had no opportunity of getting an accumulating force sufficient to rend the rock asunder.

Mr. Gates: I think that this disruptive force of crystallization is probably due more to the change in form than to an increase in volume as the content of a rounded cavity, for instance, suddenly changing to a rectangular or angular shape, would surely produce tension at many points, even though the content were no greater.

ADDITIONAL DATA ON THE CRUSHING STRENGTH OF TERRA COTTA.

BY

By R. F. Grady, St. Louis, Mo.

At the last meeting of this society I presented some results of experiments in regard to the crushing strength of terra cotta cubes. This, however, did not represent commercial conditions, or conditions under which building terra cotta is usually stressed, and in the experiments made since then it has been my aim to approach nearer to these actual conditions.

The clay used in making these test pieces was the same as that used for making enameled terra cotta, and is composed of equal parts of two local light buff clays with two-sevenths grit, all through No. 16 screen.

No special attention was given to the manufacture of these pieces, except that the presser was instructed to press the face and ribs of a uniform thickness of one inch. All test pieces were fired to cone four. All pieces had plaster of paris capping.

Sample No. 3 was not straight. The face had a convex surface.

Sample No. 10 had a face 1½ inch thick in places.

Sample No. 12 was cracked but not crushed. The pressure of 100,000 pounds was maintained about one minute, then released.

The testing machine did not record over 100,000 pounds.

These tests were made under the direction of Mr. E. E. Wall, Assistant Water Commissioner of the City of St. Louis.

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DATE	NO. OF TEST	AREA UNDER COMPRESS. SQ. INCH.	ULTIMATE STRENGTH POUNDS	POUNDS PER SQ. INCH UNDER COMPRESSION	APPROXIMATE AREA OF CROSS-SECTION UNDER COMPRESSION	POUNDS PER SQ. INCH CROSS SECTION	CAPPING	PRESSURE APPLIED AS BELOW	REMARKS
I/20.09	1.	31.72	67590	2130	18.06 sqin	3742	PLASTER		*Light Buff Clay*
"	2.	"	68180	2149	"	3775	"	PRESSURE	"
"	3.	"	58090	1831	"	3216	"		"
"	4.	"	63140	1991	"	3496	"		"
"	5.	"	63680	2007	"	3526	"		"
"	6.	"	66030	2082	"	3656	"		"
"	7.	44.86	84190	1876	22.6 sqin	3725	"		"
"	8.	"	90110	2009	"	3987	"	PRESSURE	"
"	9.	"	94560	2108	"	4184	"		"
"	10	"	100000+	2229	"	4424	"		"
"	11	"	99410	2216	"	4398	"		"
"	12	"	100000+	2229	"	4424	"		No Break, Cracks Vertical And Horizontal, None On Face.

DISCUSSION.

Mr. Binns: I will ask if there is any minimum load which terra cotta should stand, that is supposed to be a satisfactory condition?

Mr. Grady: It isn't very often that terra cotta manufacturers encounter specifications as to crushing strength.

Mr. Binns: What is the minimum strength permissible under those conditions? What is called fair?

Mr. Grady: We have encountered specifications calling for a minimum of six thousand pounds, but that is entirely unreasonable. There is no occasion ordinarily for any such strength as that.

It may be interesting to note that, if one of these terra cotta blocks was loaded with masonry having a weight of 144 lbs. per cubic foot, it would require a column of masonry of a cross section equal to the surface of the block under compression and of a height in feet represented by the figures in column No. 5. For example: Test piece No. 1 would require a column of such masonry 2,130 feet high to crush it.

Mr. Simcoe: I would like to ask Mr. Grady why he used plaster of paris to face the piece?

Mr. Grady: There is more or less irregularity in the face of the terra cotta, and we wanted to approximate the mortar bed.

Mr. Simcoe: Why not use cement?

Mr. Grady: For the reason that plaster is more easily handled.

Mr. Simcoe: We made some tests at the University of Illinois on porcelain and get much better results, that is higher tests, with the cement than with the plaster of paris. Its own strength, of course, figures in. Plaster of paris has not much strength itself.

Mr. Grady: If you examine this piece (indicating) you will find the plaster facing does not show much distress. This stood under a hundred thousand pounds pressure for about a minute.

Mr. Burt: You were testing a uniform line of samples — the same mixture?

Mr. Grady: Yes.

Mr. Burt: You did not make any comparative tests in different fires?

Mr. Grady: No, sir.

Mr. Burt: What cone was it?

Mr. Grady: Cone 4.

Mr. Burt: Was it general for the pieces to give way on the ends?

Mr. Grady: There did not seem to be any rule about that. The pieces seemed to explode. Some of them flew all around on the floor. It was not very comfortable to stand very close to them. Occasionally they would slide over here (illustrating) on the end.

Mr. Purdy: Do you find your pieces giving way on this unsupported end, or always on the edge with the rib?

Mr. Grady: In some cases it was a slip here (indicating); then again, one of those pieces on the end would jump out first; then it would go somewhere else.

(Answering further query by Mr. Purdy). I could not tell much about it except that when we would see this rib jump out, then it would go all to pieces. The edges and ribs jumped off and the back was left with a pretty sharp edge across the top where it split off.

Mr. Burt: I wish we could induce Mr. Grady to make further tests with low, medium, and high fires, showing the various crushing strengths in those three fires. Could that be done and added to this paper?

Mr. Grady: I do not see exactly the point of making such tests as that, because we do not aim to burn the material that way. These tests are made to show something of the strength of the material we manufacture. There is no doubt that a low-fired material would crush much sooner, and a high-fired material would perhaps have greater strength.

Mr. Burt: That is just the point. We do not any of us aim to have lack of uniformity, but it may vary. So

we might have a piece which is a little under-fired and be in doubt as to whether it would have a proper crushing strength. But if such tests had been made and we knew it would stand a sufficient test, we would be warranted in using it.

Mr. Grady: The strength of terra cotta is so much in excess of that necessary, ordinarily, that this does not enter into consideration very much with terra cotta men. If everything else is right, the strength takes care of itself.

A METHOD FOR DETERMINING THE MELTING POINTS OF GLAZE AND GLASS SILICATES OF THE PORCELAIN TYPE AS USED IN THE CERAMIC INDUSTRY.

BY

MAURICE BARRETT, F. C. S., Leeds, England.

At the outset it must be understood that this method is applicable only when the materials used are in the finest state of subdivision, as the size of the particles has much influence on the fusibility, although if an excessive time for the fusion be allowed this will not be so. In practical work, however, it is found more economical to have the materials in a fine state. For this reason this method is of no value for comparing the relative fusibilities of firebrick mixtures where the particles composing the mass are for the most part purposely held coarse in grain.

The opinion has been expressed that a multiple silicate fuses at a lower temperature than its components would severally fuse at, but this opinion is now held to be erroneous. What is certain is that a longer time may be necessary at a given heat to fuse the simpler silicate. The glazes commonly in use in the ceramic industry are subjected during their fusion to prolonged heat, and it has been proved synthetically that for this special industry at any rate, the assertion holds good, and the following tables are based on this.

The alumina, as is usual, is taken as unity.

Compositions approximating, in their aggregate, to the formulae will be found to fuse at the several temperatures given opposite them:

$$\left.\begin{array}{lllll} 11\ SiO_2 & : & Al_2O_3 & : & 6\ 5/7\ R.O. \\ 10\ SiO_2 & : & Al_2O_3 & : & 6\ 3/7\ R.O. \\ 9\ SiO_2 & : & Al_2O_3 & : & 6\ 1/7\ R.O. \end{array}\right\} = 1200°C$$

and so on reducing.

— 1 equiv. SiO_2 and — 2/7 equiv. R. O.

or increasing.

— 1 equiv. SiO_2 and — 2/7 equiv. R. O.

10 SiO_2	:	Al_2O_3	:	6 2/7 R. O.
9 SiO_2	:	Al_2O_3	:	6 R. O. = 1205°C
10 SiO_2	:	Al_2O_3	:	6 1/7 R. O. = 1210°C
10 SiO_2	:	Al_2O_3	:	6 R. O. = 1215°C
10 SiO_2	:	Al_2O_3	:	5 6/7 R. O. = 1220°C
10 SiO_2	:	Al_2O_3	:	5 4/7 R. O. = 1230°C

This table can by the subtraction of 2/7 RO equiv. be extended to a higher range. The RO bases are calculated as CaO equiv.

The comparison of the relative fluxing values of the RO bases with that of the CaO, which is taken as a standard or unit of comparison, shows that

1 equiv. CaO = 1/6 equiv. of K_2O
1 equiv. CaO = 1/2 equiv. of ZnO
1 equiv. CaO = 1/6 equiv. of Na_2O
1 equiv. CaO = 1 equiv. of BaO

These comprise the usual and common type of RO bases which it is possible for commercial reasons to use in the ordinary factory routine.

Table of equivalent weights and ultimate equivalents contained in the raw materials:

	SiO_2	Al_2O_3	CaO	K_2O	ZnO	
Kaolin	2	1	0	0	0 =	257
Felspar	6	1	0	1	0 =	555
Putnutze	25	2½	0	1	0 =	1925
Calcium Phosphate	0	0	3	0	0 =	310
Ground Silica Sand	1	0	0	0	0 =	60
Calcium Carbonate	0	0	1	0	0 =	100
Zinc Oxide	0	0	0	0	1 =	81
Barium Carbonate	0	0	1	0	0 =	197
Calcium Sulphate	0	0	1	0	0 =	136
Barium Sulphate	0	0	1	0	0 =	233

In order to make quite clear the method of calculation an example is given. It is required to find the melting point of an enamel composition consisting of

	Wt. Units.
Kaolin	51.40
Felspar	111.00
Calc. Phosphate	31.00
Silica Sand	72.00
Zinc Oxide	22.95

The equiv. weight of the kaolin is found from the table to be 257. This is divided into the weight units of kaolin actually in the composition which gives as a result 20 equivs. One equiv. of kaolin contains $2SiO_2$ and $1Al_2O_3$ so that 20 will contain $40SiO_2$ and $20Al_2O_3$. The other ingredients are calculated out in a similar manner, whence we obtain:

	SiO_2	Al_2O_3	CaO	K_2O	ZnO	
20 equiv. Kaolin	= 40	: 20	: 0	: 0	: 0	= 51.40
20 equiv. Felspar	= 120	: 20	: 0	: 20	: 0	= 111.00
10 equiv. Calc. Phosp.	= 0	: 0	: 30	: 0	: 0	= 31.00
120 equiv. Silica Sand	= 120	: 0	: 0	: 0	: 0	= 72.00
28⅓ equiv. Zinc Ox.	= 0	: 0	: 0	: 0	: 28⅓	= 22.95
	280	: 40	: 30	: 20	: 28⅓	

Taking Al_2O_3 as unity and approximating the RO bases to that of lime from the table of fluxing values we obtain as a final formula:

$$7\ SiO_2 \ : \ Al_2O_3 \ : \ 5\tfrac{1}{2}\ R.\ O.$$

On referring to the first table given, the fusing point of this is found to be 1205°C. This composition would not fuse into an enamel at the temperature given, as this represents simply the point of fusion.

In order to develop a perfectly fluid and finished glaze, it is found necessary to raise the temperature about 90° above the point at which the composition melts. In this case the correct firing temperature would be approximately 1295°C. An exact determination is not possible because of the physical differences met with in the molten glasses.

This method will be found to be very reliable in practical work when used for glazes of the usual type. Glazes, in which for special purposes the RO bases predominate and the silica is used as a flux, and not as a refractory agent, do not conform to the method outlined.

THE COEFFICIENT OF LINEAL EXPANSION OF PORCELAIN.

BY

A. S. WATTS, Victor, N. Y.

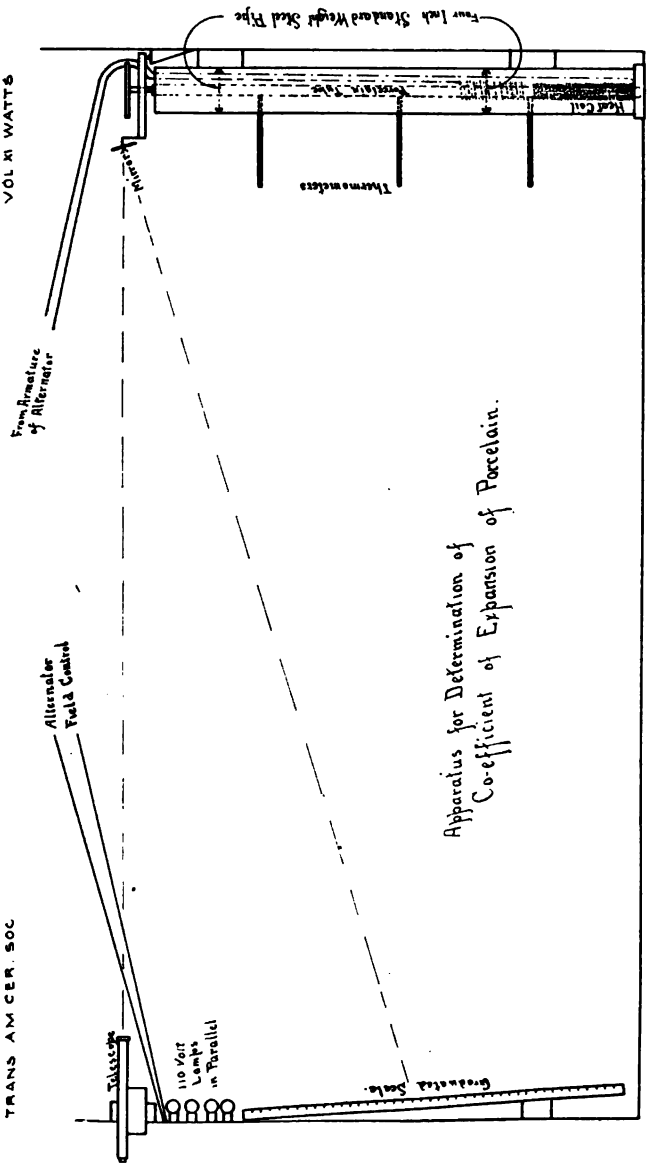
The Coefficient of Lineal Expansion of most materials is obtainable from engineering hand-books. I find, however, that the few records of the expansion coefficients of porcelain are so variable that I concluded to make a determination for myself and I offer you the data obtained with the process involved.

For the determination I used a straight unglazed porcelain tube 65¾ inches long, 1-7/16 inches outside diameter and 9/16 inch inside diameter. This tube was immersed in oil and the oil heated by means of an electrical resistance coil. The temperatures were read by means of thermometers at the two ends and in the middle of the tube. The expansion of the tube caused a lever to move. At one end of the lever was a mirror and by means of this mirror a scale was reflected to a telescope which read the expansion of the tube as exaggerated on the scale.

The scale was first standardized by means of a micrometer and by reference to this standardization the actual ratio of expansion was determined.

It was my idea to read the expansion for every five degrees, but I found that in order to have the expansion and the temperature constant, thus assuring me that the porcelain was all of an even temperature, it was necessary to maintain a uniform heat of some hours and I finally decided to make determinations for only about a half dozen temperatures and to use every precaution to see that these were correct.

I hand you the curve, as determined, in which the dotted lines indicate the rise of temperature and expansion for the entire determination, but in which no record was made of the time between readings. Usually one hour was allowed to elapse after the expansion and temperature be-


Four Inch Standard Weight Steel Pipe
Heat Coil
Thermometers
Alternator
From Armature of Alternator
Alternator Field Control
110 Volt Lamps in Parallel
Graduated Scale.
Apparatus for Determination of Co-efficient of Expansion of Porcelain.
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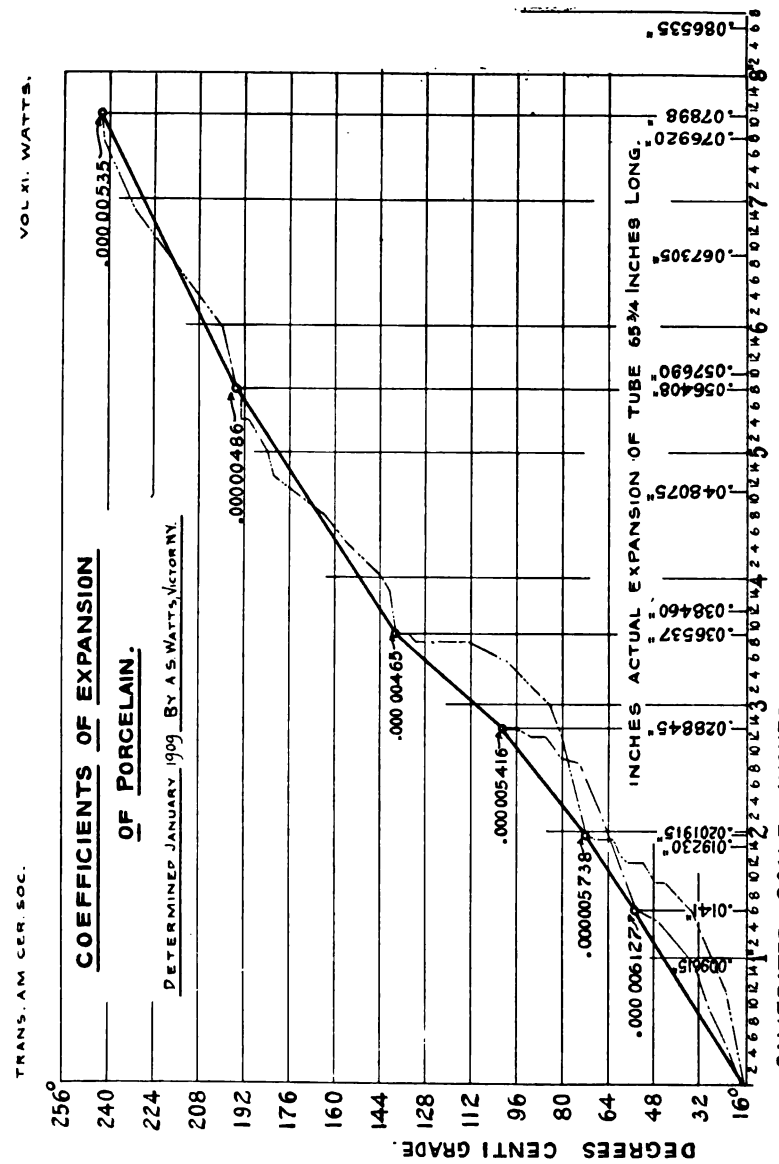
COEFFICIENTS OF EXPANSION
OF PORCELAIN.
DETERMINED JANUARY 1909 BY A.S. WATTS, VICTOR N.Y.
.000 00535
.000 00486
.000 00465
.000 00541 6
.000 00573 8
.000 00612 2
DEGREES CENTI GRADE.
256°
240
224
208
192
176
160
144
128
112
96
80
64
48
32
16°
INCHES ACTUAL EXPANSION OF TUBE 65¾ INCHES LONG.
.086535"
.078980"
.076920"
.067305"
.057690"
.056408"
.048075"
.038460"
.036537"
.028845"
.019230"
.020191 5"
.014"
.009615"
CALIBRATED SCALE INCHES.
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came constant before any final reading was made and the temperature raised for another reading.

The average of the six determinations is .000005357, which you will note is practically the same as the coefficient of the expansion for 20 to 101°C. and for 19 to 243°C. The extreme length of the tube of course reduces the danger of error which is likely to occur where a small sample is tested. The chief causes of concern in making this determination are to have your heat coil slightly removed from the porcelain, and only extending up a sufficient distance from the bottom of the tube to insure the desired amount of heat being generated.

The curve itself and the attached drawing showing the apparatus for the determination will, I think, furnish any other information desired.

DELAYED CRAZING AND SHIVERING.

WHY GLAZES CRAZE AND SHIVER AFTER REMAINING INTACT FOR YEARS.

BY

EDWARD C. STOVER, Trenton, N. J.

Crazing is usually attributed to the difference in coefficient of contraction and expansion, between the body and the glaze.

The coefficient factors of body and glaze materials have been studied and explained, and are generally comprehended and controllable and are staple factors.

But the factor of elasticity plays a very important part, and but little has been written on this phase of the subject. Dr. H. Hovestadt gives us "Young's Modulus of Elasticity" of glass materials which forms a fairly reliable basis for calculating glaze formulae:

B_2O_3	— 20	Al_2O_3	—160
SiO_2	— 65	As_2O_5	— 40
P_2O_5	— 38	BaO_2	—100
Na_2O	—100	ZnO	— 15
K_2O	— 71	PbO	— 47
CaO	—100	SnO	— 50
MgO	—600		

But owing to the differences in coefficients of the various materials whether used in bodies or glazes, it is a question if "Young's Modulus of Elasticity" of glass materials, would be applicable in calculating body formulae. Nothing short of a long series of actual tests and observations could establish this as a fact, or positively disprove it, and give us new and proper factors for our body materials. The coefficient factors have been established and are supposed to remain constant. All elastic factors are known to be unstaple.

If the coefficient of a given body and its glaze are sufficiently balanced that their difference plus their elastic factor will give a margin of safety, the glaze will remain intact until the elastic factor has decreased to or below the margin of safety point, when crazing or shivering will begin according to which way the coefficient actually differed in the beginning. It may take a short while, it may not be reached in many years, but fortunately the limits can be proven by the ice-water-boiling-water test in a comparatively short time.

DISCUSSION.

Mr. Stover: Mr. President, I will say, in this connection, that the question has been asked me why a piece of ware will remain good for say twenty years and then start to craze. I have in my hand the round cover of a soap dish, the inside of which is not crazed at all but the outside is just beginning to craze. As to the other parts of the set, some are crazed badly while others are not yet crazed.

Mr. Ashley: I will call attention to the fact that the surface which is crazed is decorated, consequently there is a larger proportion of fluxing elements on that surface than on the other side. Further, that it was the surface which came in contact with the plaster mold, consequently it had probably a larger proportion of lime than the other side. So there seems to be every reason why that surface should be crazed and not the other, as we generally expect crazing with the higher fluxes.

Mr. Stover mentions the fact that crazing can be detected by the boiling-water-ice-water test. I notice in the abstract of Mr. Cobb's paper that he will describe another test, using the repeated crystallization of sodium thiosulphate in the ware. In a recent article on the disintegration of some roofing tile in which there was some soluble calcium sulphate, it was stated that under the conditions of the roof on which the tile was used, that the calcium sul-

phate was concentrated at one end of the tile, till it was found there was five per cent in that end. Those tile broke up at that end by the crystallization of the calcium sulphate at the upper end and where evaporation took place under sheltered conditions. In my paper on "Testing of the Raw Materials for Whiteware Pottery," Vol. IX, p. 59, I described Mr. C. H. Welker's accelerated test for crazing, in which a piece of ware is boiled 8 hours in saturated salt water, then thoroughly dried out at gentle heat. I suggested that the same test might be applied to wall tile, substituting for the salt the plaster in which they were to be set. It seems to show, then, that in the years of use domestic wear gets, various substances will be absorbed, concentrated, and crystallized and thus upset the equilibrium which existed at the time the ware came out of the kiln; and to these altered conditions, as well as to the elasticity breaking down, might be attributed the delayed crazing.

Mr. Watts: Mr. Ashley made the statement that there was some lime possibly absorbed by the ware, due to contact with the mold. Would it not be more likely that the mold would draw from the ware any soluble alkali salt it contained, rather than that the ware would take from the mold any lime which the mold carried? Have we any evidence that in the length of time the ware would be in the mold, the action would be sufficiently extended so that the ware would begin to draw from the mold? Would it not rather be the case that the mold would draw from the ware?

Mr. Ashley: In a paper on Pottery Plaster, Vol. X, p. 87, I gave the results of experiments in making ware in a dry mold and quickly drying it in the pottery stove room, as against forming the ware in a wet mold, and allowing it to stand around the room with slow drying. I found in the latter case the absorption of the ware for water was cut down one per cent, showing a greater vitreousness of the ware with the longer contact with the damp mold and consequently an absorption of calcium from the mold.

Mr. Jackson: I think in the case in point, the crazing is due to being heavy-dipped. If you will notice, the two curved surfaces have the most glaze on, naturally, and they are the only two points crazed.

Mr. Stover: I think a closer observation of the piece will disprove that, as on the under side on the edge it is starting to craze. Four or five years ago, the whole toilet set had no sign of crazing, and now many pieces are crazed inside and out; so the decorated feature will not explain the crazing where there is no decoration. In regard to the explanation about the ware taking up some foreign substance and delayed crazing being caused by that, while it might be one factor, I do not think it is as important a factor as the elasticity factor. There is another case of a closet which had been in use twenty or twenty-five years before those parts in actual use began to craze, and before those parts out of sight crazed, but in two or three years more they did.

Mr. Binns: I think Mr. Stover is undoubtedly right and we are apt to switch off into something we do not mean. We are dealing particularly with the question of elasticity here. I am sure every substance grows tired. The rubber in your garters, braces or what not grows tired and eventually loses its elasticity. If there happens to be ever so slight a disagreement between body and glaze, it may not be apparent as long as the glaze has elasticity to overcome it; but eventually the glaze gets "tired" and cracks.

I would like to ask Mr. Stover if he ever saw a case of delayed shivering?

Mr. Stover: I had some samples but could not get hold of them to bring with me. One was an old underglazed blue plate which had begun to shiver, tho it did not show it at first, but I could not find it. If this elasticity factor plays a part in one it would in another, with delayed shivering at one end and delayed crazing at the other.

Mr. Bowers: I will ask Mr. Stover whether the articles in question might not have been in the dark for some

time and then brought into the light? If kept in the dark and then brought into sunlight it would cause molecular rearrangement. Crystallization of the material, which had been delayed according to the composition of the glaze, might take five or twenty years.

Mr. Stover: No. In constant use.

A METHOD OF OVERCOMING THE SULPHUR PROBLEM.

BY

H. B. WELLS, Ironton, Ohio.

The presence of sulphur in clays and its elimination with good results has been and will be a subject of much discussion. Sulphur probably causes more trouble than any other element occurring in clays, especially so where the product manufactured will not justify an expensive preparation of the clay. It is not only troublesome during the process of burning, where it causes discoloration and distortion in defective burning, but in many cases where the burning has been successful sulphur is the cause of surface discoloration or scum. This latter case we will not touch upon at this time, as that is a problem by itself, but we will deal with the burning only.

We have had papers read before the Society covering the carbon and sulphur problem which have been based on laboratory experiments and which have been an invaluable guide in overcoming the trouble arising from these two elements. What is to follow is based on the problem as it confronts us in a commercial way. The method of experimentation is not a very commendable one as it is very expensive, but the plant where the experiments were made, like many others which manufacture crude ware, did not have the luxuries of a laboratory, a test kiln and a pyrometer, so there was no other alternative. In fact a test kiln would not have been of much value to us, as the effect of the mass would have been lost, which was very important.

The plant to which the writer refers is operated by the stiff-mud process, manufacturing brick and fireproofing. There being practically no difficulty in making either

of these products and getting them into the kilns, we will confine our remarks to the burning. There was also no difference in the burning of these two products, with the exception of an extension of time for the bricks, so that the general principles apply to both. The wares were burned in round down-draft kilns 30 feet in diameter.

The system of burning which had been used previous to our experiments was to start with low fires and gradually increase them till the burning was completed. During a great part of the time volumes of sulphur fumes would evolve from various parts of the kilns and from the stack. The fumes were still evident for several hours after the firing had been completed. The results of this method were anything but satisfactory, as a large per cent of the product was taken out of the kilns in chunks and carted to the dump. The drawing would show that the contents for about four feet in was a little underburnt, then for a few feet the ware would be well matured while the center was very much over-burnt, being stuck together and out of shape. By breaking a piece of the over-burnt ware, it showed a very black spongy core from which the conclusion could be easily drawn that some gases had formed on the inside and could not escape on account of the outside shrinking too soon and closing up the pores.

We are somewhat handicapped by not having a total analysis of the clay, which is of Cretaceous origin having pebbles of iron sulphide distributed all through the bed, but we are fortunate enough to know the sulphur content, which is 1.82%. Since the scumming of the product is by no means excessive it is safe to say that the larger part of the sulphur is present in the form of FeS_2.

Knowing from past experience that the sulphur in the FeS_2 oxidizes at two stages, the first molecule at about 400 C. while the last remains until about 900 C., and that this oxidation will take place properly by a careful regulation of the air, we started to work by bringing a kiln up to a dull red heat and letting the fires die down at this point, merely keeping them alive, thinking that by so doing the

oxidation of the sulphur would take place at a slow rate. We did not attempt to close up the fire boxes and other air inlets, not wishing the heat to go back too far, but before we realized what was going on, the kiln had attained a bright red heat. Ceasing to fire the furnaces proved of no avail, as the heat in the kiln became more intense in spite of all we could do. No more firing was done until the center of the kiln, which was the hottest, had cooled down, when enough fuel was added to finish the outside courses.

Upon drawing we found that the only advance made was that there was no under-burnt material.

Our next step was to bring a kiln up to a dull red heat, pull the fires and close up the fire boxes leaving them in this manner until the kiln was again ready for the fire to be started for maturing the ware. As there was some difference in the floor construction of some of the kilns, this system was tried on several of them but the result was the same in each case — an over-burnt center, but of not quite so great an area as the first trial. The top courses were well burnt but the middle and bottom were as much distorted as before.

The top being good with no improvement in the middle and bottom of the center, led us to believe that the air, as it passed through the top courses, became preheated and more efficient, causing the oxidation in the bottom to take place too rapidly, so we made some experiments with the setting, that is, set the bottom courses more open, thus allowing a greater draft, having a tendency to carry the air through much faster and not allowing it to become so hot. This did not have the desired effect, as the over-burnt middle and bottom of the center were still there.

On the next kiln we carried the problem one step farther by closing the kiln before it had attained a dull red heat. As we had no pyrometer to indicate the temperature, this had to be done by guesswork. Knowing the time that usually elapsed between the evolution of the first molecule of sulphur and the attainment of a dull red heat, we di-

vided this time in half and closed the kiln up at this midway point.

The kiln advanced at a much slower rate than in any of the previous burns, but even this time the kiln reached a bright red heat in the bottom and middle, but not so much as before. The drawing showed a decided improvement but a portion of the kiln was still unmastered.

The next kiln was closed up as soon as there was evidence of sulphur fumes. We were a little in doubt as to whether the kiln would advance in heat, being closed up at such an early stage, but, to our surprise, it did increase very slowly and at a rather uniform rate. It gained an intense heat in the bottom but covering less area than any we had tried so far. On drawing, we found a bad place where we had expected it from our external observations.

What to do next was rather perplexing, but having come so near the solution of the problem, we were not willing to give up. The central part of the kilns being the point of contention, we concluded that if it were possible to admit air at this point at a low temperature and prevent the hot gases from passing through this one central point, we would have mastered the situation. Being willing to try most anything, the exhaust fan, which was connected with all the kilns, was put into play. We handled a kiln as before except that the gases were turned into the fan instead of the stack during the oxidation period, thinking that the gases and air passing through at a rapid rate would have a tendency to keep the temperature down and cause a slow oxidation. Such was not the case, however, as the result was nearly as disastrous as some of our first trials.

At this point we began to think that we would be unable to burn the clay in down-draft kilns. Knowing that the gases were not under very accurate control in the up-draft type, our attention was turned to reversible kilns, and we conceived a plan to carry out the idea with the kilns we had, which was to open up the top of the kilns during the oxidation period. This would allow the gases

from the top courses of the ware to escape first and, by going directly into the atmosphere, they would not pass through any of the other ware and give off heat which would cause a rapid oxidation in other parts of the kiln.

At first we were in doubt as to what point in the oxidation we should open up the top of the kiln, but, as we were more willing to increase our fuel bill, if necessary, rather than endanger the ware, we brought the next kiln up to the ignition point of sulphur, when the fires were allowed to die out and the fire boxes closed up, the openings in the crown uncovered and the gases shut off from the stack entirely. The heat advanced rather slowly but it moved gradually from the outer courses toward the center, giving no evidence of becoming too hot at any point. The sulphur gases kept passing off for several hours after the black core had all disappeared from the trials. When they had ceased, the top of the kiln was closed, damper opened to the stack, and fire started and carried in the usual manner for the completion of the burning.

The result of this method was practically a uniform burn throughout. The bad place which we had been fighting in the center had all disappeared. No sulphur fumes could be seen after the burning was complete.

During our first experiments, we thought that the evolution of sulphur after the firing had ceased was due to having the dead coals in the fire box. This undoubtedly produced some of the gas but, upon cleaning the fire on several of the kilns at the end of the burning, there was no apparent reduction in the volume of gas. This showed conclusively that the sulphur in the clay was the cause of our trouble.

There is no question but that the carbon played some part in the imperfect oxidation, but the black core, which is largely due to carbon, disappeared long before the evolution of the sulphur ceased. As the ignition point of the carbon, which is about 700°C., is midway between the ignition points of the two parts of the sulphur, the former would take care of itself if we could control the latter.

After having satisfied ourselves that the above method was successful by burning several kilns in the same manner, we came face to face with another obstacle, which was that we were not turning our kilns over fast enough to keep up with the capacity of the plant. This called for further experimenting, the outcome of which resulted in the covering of the top of the kiln before all of the sulphur had passed off, which advanced the heat in the bottom much sooner than we could produce the same heat from the fire boxes with no sulphur in that part of the kilns. Much care had to be exercised in judging the proper time for action in order not to start the fires too soon and ruin some of the ware. After watching several kilns very closely, we were able to pass this point with safety.

Our experiments resulted in our adopting the last mentioned system which, to the writer's knowledge, has been used for two years with much satisfaction. It is not, however, a commendable method for all clays which contain sulphur; but where they contain a very large amount, it is one solution of the problem.

THE EFFECTS OF ALUMINA ON GLASS.

BY

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It is to be regretted that there is not a more general perception among glass-makers and glass manufacturers of the actual components which go to make up a piece of glass, and what physical properties each of these components give to the finished product.

I say that this is not understood among glass manufacturers — perhaps I may also say that this is not well understood by any one, as there has been little or no scientific investigation made of this character, or at least, if there has been, it has not yet eked out and become public property.

The nearest to anything of this character which is published at present, are the experiments of Wieper, Winkelman and Schott, and while the results obtained by them are very satisfactory and highly technical, they apply more particularly to those glasses used in optical work, or in the making of chemical and scientific apparatus.

My own experience has been that while their results may be considered as authentic and indicate an average of what might be obtained under ideal conditions, they do not give us a fair representation, or representative basis, on which to base our calculations in the determination of the physical properties of glass produced under practical manufacturing or operating conditions, particularly so when the same is made and melted in open tank furnaces.

As has been shown in another paper before this Society, the action of fire, and effects of temperature during the melting operation, have much to do with the physical properties of the glass; and inasmuch as it is a very difficult problem to calculate what the conditions are going to be, it would seem logical that we should endeavor to get a glass which would be as little effected by varying conditions as possible. Why this is not considered, and has

not been done before, is due, I believe, to the lack of knowledge by the practical man as to the actual chemical components entering into the finished material. He has become accustomed to believing that all of his materials must be in a certain condition of purity, and the ingredient which he has most regard for is his sand. This sand he insists upon having washed and rewashed, in order to remove the loam and extraneous matter, until he has nothing left but pure silica, or as near pure as possible. However, I venture to made the radical statement, that in washing the sand and removing the loam he is removing one of the most valuable ingredients contained in any of his raw materials, provided, of course, that this does not exist in too great excess.

This loam contains alumina in a more or less hydrated condition, and combines the soda, silica and lime in such a manner as to be immediately and perfectly assimilated when melted with the other ingredients that go to make up the finished metal. Alumina has the peculiar property, when existing in quantities of approximately 3 per cent, of acting as a vehicle for forming combinations between the silica and lime, and silica and soda, and I assume takes the place of either an acid or base, thereby neutralizing that component that may exist in excess, and so to speak, maintaining a state of chemical equilibrium, which otherwise can not, or does not, exist.

As stated above, when existing in proportions of about 3 per cent, we would have a sufficient quantity of alumina, or if the proportion of raw material should be anywhere near that which would produce an eutectic, we would have an amount which would satisfactorily fill the above requirements when needed, or be negligible when not required.

Another property which alumina has, and which is very beneficial in making glass in open tank furnaces, or where brought in direct action with the fire, is that of facilitating the making of a homogeneous, isomorphous body. Just what the reasons for this are, I have been unable

to determine, and have only found that when alumina exists to the extent of 3 or 4 per cent in a finished glass, this glass is not near as susceptible to the carbonizing or reducing action of the fire, or to the formation of cords and strings, or production of a laminated condition, whether soda or salt cake be used for supplying the soda content.

In making a glass without alumina or with an alumina content of .6 per cent, whether the same be made of salt cake or soda ash; when, in a semi-finished state, it passes into the highly reducing gases, or gases carrying free carbon, we will have a condition which has caused a considerable assimilation of this carbon in a form of carbide of sodium, this being readily discernable, even at high temperatures, as a dark-colored, greenish streak on the surface of the glass. Because of these streaks the glass will have lost in tensile strength, will be found to be lower in its modulus of rupture, its viscosity will be considerable lower, and in fact it will be poorer in quality in every respect than that glass which contains from 3 to 4 per cent of alumina.

Alumina furnishes another very beneficial property, particularly in the manufacture of glass in molds, or under machine conditions, wherein the surface is rapidly chilled, that is, it has a tendency to increase the coefficient surface tension per degree of temperature. Or in other words, when glass containing 3, 4 or 5 per cent of alumina has been gathered, or ladled, from a mass of open metal at a temperature of, say 1150 degrees C., its surface immediately becomes lower in temperature, and at that drop in temperature, which will invariably follow when allowed to remain in open air, and which will approximate 825 degrees, it will be found that the skin, or over-lying stratum, will be very tenacious. Therefore, whenever glass of this character is gathered, or ladled into molds, and pressed or blown, it has less tendency to take the imperfections of the molds, or other objects with which it may come in contact, but at the same time this film, or coating, is plastic and sufficiently pliable to be forced into any desired shape. In the manu-

facture of bottles particularly, alumina is a valuable factor because of its reduction of the coefficient of expansion and increasing the tenacity of the glass, and also because of its furnishing that additional property cited above, namely free working, and not readily taking mold imperfections.

Further, alumina facilitates annealing to an extent whereby a bottle will stand much more severe usage without breaking, and it also adds to the annealing properties of the glass to an extent which does not require the annealing to be conducted in as careful a manner as should be done with other glass, if a first-class product is to be produced.

Alumina has one property, however, which I have found in my experiments requires it to be handled with some care, and that is it does not mix well with other glass to form a perfectly homogeneous glass, free from cords, and care must be exercised to see that all cullet used in the making should be filled with the batch materials in not too large quantities.

I have presented some of these points for discussion with the idea in view that there may be some members of this Society who have had experience in the making of glass from unwashed sand, and to ascertain whether such sand has given any trouble. If so, I should be much interested to know what these troubles were, and the conditions under which they occurred. However, my prime object in presenting this discussion, is to get some manufacturer to take a fair quality of sand rock, crush it and use it under comparatively normal conditions, and thereby eliminate the useless expense of throwing away one of the most valuable constituents, in my opinion, of our raw materials, and I feel sure that he will have found a considerable improvement in the quality and the working properties of his metal.

THE ALLOWABLE LIMIT OF VARIATION IN THE INGREDIENTS OF ENAMELS FOR SHEET STEEL.

BY

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This paper consists of a revision of a thesis presented for graduation from the Ohio State University.

At the time the original thesis was written, the writer had had no practical experience in the production of enameled iron ware, but had been closely connected with firms producing this ware for several years. Still, the old rule applies, experience is our best teacher, and although the writer had been a close observer of the process of manufacturing this ware, there were a few of the most essential points which he had not learned and which can only be learned by the actual production of the ware under varying circumstances.

Two of these points are:

(1). The proper tempering of the slip before dipping, i. e., making the slip of such a consistency that the enamel will be neither too thick nor too thin and will not run down the the sides of the ware after dipping.

(2) The proper burning of the ware.

Because of the fact that the writer did not understand the importance of both of these points, and lacked experience in handling the ware, some of the results obtained in the following described experiments were misleading. The conclusions drawn in the original thesis were nearly all correct, so far as the proper translation of the data shown from the test pieces was concerned, but experience has shown that these data were partly misleading, hence this revision is made necessary.

It is beyond the scope of this paper to enter into the history of the art of enameling sheet steel, but it may be

said briefly that the status of the industry today is very similar to that of most of the clay-working industries a few years ago. The industry is almost entirely in the hands of practical men without technical training. The development of the industry in the last decade has been very marked from a quantitative standpoint, but qualitatively there has been very little change in the output. The formulae used at present have been handed down from the early history of the industry and, with perhaps a few modifications, the enamels produced today are the same as those produced twenty-five years ago.

Within the last decade the demand for this class of ware has increased enormously and the result is that numerous plants have sprung up over the country and are producing ware—some good, some very poor—and at present the supply is greater than the demand. This means that within a very few years it will be a "survival of the fittest," and that the practical man who does not know how to modify his formulae and methods of application so as to produce the ware cheaper will have to step down and out and give place to the technically trained engineer.

CLASSIFICATION.

The industries manufacturing wares of metals covered with enamels may be conveniently classified under four heads, viz.:

Cast Iron Sanitary ware.
Sheet Steel and Sheet Iron utensils.
Enameled Watch Dials.
Ornamental or Art wares.

The first two of these are by far the most important and both are rapidly growing industries at the present time. The Cast Iron Sanitary ware industry has for its basis a cast iron shape, to which is applied a glassy coating or enamel. The sheet steel of Sheet Steel Utensil industry has for its basis a sheet iron or sheet steel shape to which is applied a glassy coating or enamel. Although these may

seem at first thought to be very similar, still a little study will show that the circumstances require the methods of manufacture to be widely different in some respects.

The wares made from cast iron are usually large and heavy. The iron has a rough, granular surface and usually contains many impurities. This class of ware is required to be strong, and the enamel must possess sufficient beauty and stability to make the ware sell.

The wares made from sheet iron or steel are usually small and light in weight. The metal has a smooth hard surface and is usually free from undesirable impurities. The strength of this ware is of minor importance, but the beauty and stability of the enamels are more important than those of the cast iron industry.

This brief comparison is sufficient to show that although the two industries have many points in common, still there must necessarily be many points wherein they are different. In the cast iron industry the shapes are cast, while in the sheet iron industry they are stamped from the sheet metal. The method of cleaning the iron preparatory to applying the enamel is very similar in both industries. In the cast iron industry the enamel is applied in the form of a dry powder, excepting the ground coat, which is frequently slushed on, while in the sheet iron industry it is applied as a slip.

The composition of the enamels in the two industries is very similar in some respects while widely different in others. The relation of acid to base does not differ widely in general but the composition of the RO is often quite different. The cast iron enamels may use lead for a flux but the sheet iron enameler can not use lead because of its poisonous nature. This brief outline is sufficient to give a general idea of the relation existing between the two industries. For a further study of the cast iron sanitary ware industry the reader is referred to Vol. IX, of the *Transactions of the American Ceramic Society*, which contains a paper written by Frank H. Riddle on the "Types of Enam-

els Used for Enameling Cast Iron Sanitary Ware." My work was confined to the sheet steel enameling industry.

METHOD OF MANUFACTURE.

The following is a brief outline of the method of manufacturing enameled cooking utensils and other household articles from sheet iron or steel.

The Steel. The steel used for enameled ware is purchased from the steel mills as enamel stock. It is usually, and should always be, specially prepared. It should contain a smaller amount of impurities, such as sulphur, phosphorus and carbon, than steel for other purposes. The sulphur and carbon should be low because they tend to oxidize during the fusion of the enamel and, coming off as a gas, produce pin holes. The phosphorus must be low because it makes the steel brittle. The steel must be ductile in order to stand pressing into shape without rupture. It must be very homogeneous, because if it is not there will be hard streaks and soft streaks and when the enamel is fused onto it, there will be streaks of pin holes, and blister. A low grade steel very often shows streaks of various colors and appears to be made of pieces patched together. This steel is composed of scrap of all kinds, good and bad, hard and soft, thrown together, heated, and rolled into sheets. It is very undesirable for enameling purposes. Steel for enameling should be the very highest quality of hot-rolled steel. Summarizing, we may say that the steel best suited for this class of work is a very high quality, low carbon, soft steel.

The metal is rolled into sheets, varying in thickness from 1/20 to 1/50 of an inch. It is then cut into squares varying in size according to the article to be made from it. It is then annealed by heating to dull red heat, after which it is ready for shipment to the factory.

Open-hearth and Bessemer steel are both used but the open-hearth gives the best results. It has been a little more expensive than the Bessemer but at present the price of

the two grades is the same. The open-hearth is always used for deep ware where high ductility is most required in stamping.

Taking up the different operations of the process of manufacture in the order of their occurrence we have:

Blanking. By this is meant the cutting of the sheet into the proper form and size, so that when drawn there will be sufficient stock remaining on the edge to produce a bead or other appropriate finish. By far the greater number of steel shapes are circular and these circular shapes require a circular blank. They are cut 1, 2 or 3 at a time. The machine in which the circles are cut consists of a device for holding the sheet so that it may revolve around its center as an axis and a pair of small circular shears which are made to revolve by power.

Oiling the Blanks. The blanks are taken from the circular cutter and passed between two rolls that are covered with felt. The felt is kept well saturated with enameling oil, and as the blanks pass through they are coated with a thin film of oil. The object of this process is to decrease the friction between the steel and the die in the process of drawing.

Drawing into Shapes. By this process the blank is pressed into the desired form. The process sometimes requires five or even more operations through the press, depending on the depth of the shape when complete. For shallow ware, one or two operations is sufficient. Where a shape requires three or more operations, it is usually necessary to anneal the steel one or more times before the drawing process can be completed. The reason for this is that as the steel is pressed from one shape into another it becomes brittle and unless it is softened by annealing it tears or ruptures before the drawing is complete. The term "shape" is applied to any piece of ware that has gone through the trimmer and beader and is ready for the ears and handles, or the cleaning process in the case no ears or handles are required.

Spinning. The process of spinning is required on all

shapes that are not smooth after the drawing process. In the drawing of certain shapes, spinning is always necessitated, while in others spinning is never required. The object of spinning is simply to get rid of any wrinkles or creases produced in the drawing process. A steel punch, similar to the last punch used in the drawing process, is fastened on the end of a revolving shaft. The piece to be spun is placed over the punch which it fits neatly and is clamped on so as to revolve with it. As the shape thus revolves, a hardened steel wheel with rounded edge and free to revolve is slowly moved up to the shape and when it touches it is slowly and uniformly moved so that the edge of the wheel is constantly in contact with the shape. When the entire surface of the shape has been gone over, the wheel is withdrawn from the punch, perfectly smooth except for the marks made by the spinning wheel, which are negligible.

Trimming. After spinning, the piece is taken to the trimmer where the excess stock is cut off the edge. This is accomplished by revolving the shape as in spinning and bringing a pair of circular shears in contact with it which trim off the excess steel.

Beading. After the excess stock is cut off, a bead is turned on the edge to give finish and strength to the shape.

Putting on Ears and Handles. With many of the shapes, the turning of the bead is the last operation before cleaning the steel for the enamels. All shapes requiring handles or ears for bails are taken to the riveters after the bead is turned on, and the handles or ears are riveted on the shape.

Cleaning the Steel. With the handles or ears in place, the shape is now ready to be cleaned, preparatory to applying the enamel. The first operation in cleaning the steel is called scaling. It consists in placing the shape in the furnace and heating it to a dull redness. This burns all the oil and other combustibles off the steel which the pickling acid might not remove and leaves the steel coated

with a thin layer of iron oxide. This oxide is removed by pickling the steel in dilute acid. At present, hydrochloric acid is generally used but we find that sulphuric acid may be used with equally good results. The shapes are put in the acid bath and left there until the iron scale has been removed. They are then thoroughly washed in clean water, from which they are transferred to a tub of boiling water which is kept alkaline by use of soda ash. They are taken from the soda bath and immediately placed on a hot plate or other drying device and dried as rapidly as possible. When dry they are delivered to the first coat dippers and the first coat of enamel is applied as soon as possible to prevent the steel from being allowed to rust. After dipping in the first coat of enamel, the ware is immediately placed in the dryer and dried rapidly to prevent rusting.

Burning. The ware is usually burned in muffle kilns. The temperature used in burning varies from 750° to 1000°C. and the time varies from 4 minutes to 10 minutes. The time and temperature required depends on the enamel. The treatment given the ground coat should always be more severe than that given any subsequent coat. The ware is supported on iron pins or other convenient supports and put into the kiln by means of a fork supported on wheels. One charge consists of from twenty to thirty pieces of ware. In order to get the ware in and out of the kiln it is necessary to raise a large door which opens the entire end of the muffle. This arrangement limits the temperature that can be maintained in the kilns but is very convenient and efficient for burning this class of ware.

ENAMELS.

The enamels used in this industry, although closely related to glazes in some respects, are still widely different from them in others. The greatest difference between the two is in the more complex formulae used for enamels.

They invariably contain a greater number of different ingredients than glazes, although the ultimate composition of the glass resulting from the two mixtures is usually quite similar.

Comparing the materials used for the production of enamels and the commonest types of glazes, we find the following:

RAW LEAD GLAZES.	FRITTED GLAZES.	ENAMELS.
Feldspar	Feldspar	Feldspar
Flint	Flint	Flint
Clay	Clay	Clay
Calcium Carbonate	Calcium Carbonate	Calcium Carbonate
Lead Compounds	Lead Compounds	Sodium Carbonate
	Sodium Carbonate	Borax
	Borax	Cryolite
		Fluorspar
		Salt Petre
		Coloring Oxide

These lists represent the materials ordinarily entering into the two commonest types of glazes and enamels. Comparing the formulae of Raw Lead Glazes, Fritted Glazes and Enamels, we find the following:

Raw Lead Glazes.

.7 PbO
.15 CaO .2 Al_2O_3 1.6 SiO_2
.15 K_2O

Fritted Glazes.

.25 KNaO
.50 CaO .3Al_2O_3 2.75 SiO_2
.25 PbO .25 B_2O_3

Enamels.

.15 K_2O
.60 Na_2O .2 Al_2O_3 1.6 SiO_2
.24 CaO .4 B_2O_3
.01 coloring matter

These formulae represent about the average composition of these materials. Since the enamels are burned in from four to ten minutes at a temperature of from 750° to 1000°, it is evident that the enamel must be very easily fusible. It is not permissible in the sheet steel enameled industry to use lead as a flux because of its poisonous nature. There is no doubt but that a small amount could

be used without danger, but the public is prejudiced against it, and enameled ware containing lead is difficult to sell if the facts are known.

The degree of fritting the enamels is so extensive that it is quite impossible to retain much lead, and since the atmosphere of the frit furnace is invariably reducing, the PbO reduces to metallic lead, and the writer has taken off frits of white glaze in which there were numerous globules of metallic lead. During the burning of these enamels the lead reoxidizes, forming an undesirable yellowish red speck in the white enamel. This could no doubt be overcome by properly oxidizing the enamel batch in fritting, but sheet iron enamelers seldom use lead and no attempt has been made as yet to overcome this difficulty.

Since cast iron enamlers use lead in their formulae, it is probable that their frit furnaces are kept oxidizing or that they have strong oxidizing agents in their formulae.

The enameler can resort to boric acid to soften his enamel, but the limit of this is soon reached in wares of the grade under consideration because of the cost and the properties which it imparts to the enamel.

Comparing the formulae of enamels and fritted glazes we see that the ratio of B_2O_3 to SiO_2 in enamels is higher than in the fritted glazes, although this ratio in the latter often runs as high as 1:5.

The total acidity of the enamel is less than that of the glaze. The PbO of the glaze is replaced by alkalies which are good fluxes, but less powerful than PbO. These comparisons show that the enamel is more fusible than the glaze in general, but they do not account for as great a difference in fusibility as actually exists. The two greatest factors in causing the great difference in fusibility are:

(1) The more fusible nature of the raw materials entering the enamels.

(2) The fact that in producing the enamels, practically everything is fritted, while in producing the glaze

the frit only composes about 60 per cent of the total glaze batch.

Enamel wares may be conveniently divided into three classes, namely (1) one-coat ware, (2) two-coat ware, (3) three-coat ware.

ONE-COAT WARE.

It has only been within the last few years that this class of ware has been found on the market. As the name implies, it consists in the steel form to which is applied one coat of enamel. All of the cheaper ware on the market is of this class, although part of the one-coat ware is as good as much of the two or three-coat ware, but most of it is poor in quality. The process of making it has been patented, but it is very easily produced. Some experiments were performed along this line and the ware produced was fully as good as most of that found on the market. An examination of a piece of one-coat ware shows that the enamel consists of an opaque white coat containing numerous brown spots or streaks. In the experiments performed, an opaque white enamel was applied to the steel and then allowed to stand in the air to dry so that the steel would rust before drying. To facilitate rusting the steel was not dipped in an alkaline bath after pickling but was taken directly from the acid and dipped in the enamel. The rust spots sometimes show through the enamel after drying, sometimes they are invisible but they always show up after the ware is burnt. The rust spots are the brown spots on the finished ware, caused by the iron oxide attacking the enamel which does not flow and is not fluid long enough to allow the coloration to become uniform over the surface. The writer believes that with the proper care a very high grade and serviceable class of ware can be produced in this way.

TWO-COAT WARE.

This class of ware is just coming into prominence at the present time. It is the result of an attempt to produce

white enamel ware cheaper than by the use of three coats. Heretofore the practice has always been to apply three coats of white to produce a good white piece of enamel ware and it may be said that this is still the general practice, but this makes the ware rather expensive and competition is compelling manufacturers to cheapen their product. Hence some firms are attempting to produce two-coat white ware. The attempt has not been entirely successful as yet, although some fairly good ware has been made by this process. The only point wherein two-coat ware is inferior to three-coat ware is in its whiteness. When the white coat is applied thick enough to produce a good white cover with one coat, the enamel "crawls" or draws up into beads, instead of spreading out in a thin uniform coat, and thus produces defective ware. When sufficient tin oxide is added to the enamel to give a good white cover with a moderate application, the enamel loses part of its lustre and the cost is nearly as great as three-coat ware.

A very nice one-coat white can be produced by using ZnO and Sb_2O_3 in the frit and adding the SnO_2 now as usual. It is necessary to apply this coat a little heavier than we would if we were using two coats but if the raw clay is kept low, no trouble from crawling will result.

Two-coat ware is superior to three-coat ware in that it is lighter in weight than the three-coat ware and hence is likely to stand more handling than the latter which, because of its own weight, is likely to have the enamel knocked off in a short time and consequently be short lived unless of a very superior quality.

THREE-COAT WARE.

In this class fall all of the better grades of enamel ware or at least all of the higher priced ware, but the fact is that much of the three-coat ware on the market is less serviceable than a part of the one-coat ware and two-coat ware. However, since the three-coat ware costs more to manufacture and is more artistic than the other grades, it must command a higher price.

This class of ware consists of a steel form, to which is applied a ground coat of two or more cover coats, the latter being either white or colored. Sometimes a colored enamel is sprinkled on the ware while the last coat of white is still wet and by shaking slightly, the marbleized effect, which is often seen on the market, is produced. This class of ware will be discussed under the headings (1) ground coats (2) cover coats.

Ground Coats. The ground coat is the vital part of every piece of enamel ware. It is the coat applied directly to the steel and hence the one forming the bond between the steel and the subsequent coats. The life of every piece of enamel ware depends directly on the efficiency of this bond. Of course, when enamel wares are used for special purposes which require an enamel of special quality as regards acidity or basicity, then the enamel may fail by being eaten off if not of the proper quality, but this ware is seldom subjected to such use. Nearly every piece of enamel ware fails by rupture of the bond between the enamel and the steel, and hence it is essential that the ground coat adhere tenaceously to the steel. This is the only property absolutely essential in the ground coat.

The next property of the ground coat in importance is its fusing point. The absolute fusing point of this coat is not so important as is the relation existing between its fusing point and that of the subsequent coats applied. The ground coat must fuse at a temperature higher than any subsequent coat and still it must soften enough while burning the cover coats to form a good bond between them. If the ground coat fuses while burning the cover enamels, it is certain to cause pinholed and defective ware. From these facts we conclude that the ground coat must have a long range of fusion. That is, it must soften under the heat treatment given the cover coats but it must not be affected enough to become liquid or give off gases. Hence, we see that adjustment of the time and temperature of burning the different coats is quite a delicate operation, and the cor-

rection of the melting temperature of the different coats while still maintaining their other desirable points is an operation requiring some knowledge of the materials entering into the enamels. This is one of the difficulties which practical men are often unable to overcome and which causes much poor ware to be made.

Another desirable property of the ground coat is that it have a good lustre. If the ground coat is smooth it is comparatively easy to maintain this property in the subsequent coats, but if the ground coat is rough it seems to impart this property to the subsequent coats. The writer is unable to explain this phenomenon, but it was quite marked in the series of experiments herein described. The color of the ground coat has aways been of subordinate importance, although it may become more important in the production of two-coat white ware. It is nearly always dark in color, varying from light brown to black. Blue is quite commonly used probably because it aids in intensifying the white of the subsequent coat. It also has the advantage of changing color during burning, the iron taken up from the steel destroying the blue cobalt color. The ground coat is considered well burnt when the blue color is no longer visible. It seems to be quite generally believed that CoO has a great affinity for iron and that a good ground coat can not be made without using CoO. The writer has experimented a little along this line and feels perfectly safe in stating that this belief is ungrounded. The dark color of this coat is partly due to iron taken from the steel and partly due to pigments added, the most common of which are cobalt, manganese and nickel.

As stated above, enamel ware usually fails by rupture of the bond between the enamel and the steel. A good test of a ground coat is to subject the ware to blows. The best ware when subjected to blows will stand a pretty severe test and when it does fail, the surface of the steel where the enamel has failed will still have strips or patches of enamel adhering to it, or possibly the outer coat of

enamel will chip off from the ground coat. The poorer grades of ware when subjected to blows will soon fail, the enamel flying off leaving large, bright patches of clean steel. Some test the ware by bending the steel and think a good enamel should stand the bending of the steel around a small rod. The writer does not consider this either a fair or an efficient test. This test introduces conditions, to which enamel wares are never subjected, and to pass the test the enamel would need properties which its very nature forbids its having. Another test sometimes applied to enamel ware is to heat it to a high temperature and then plunge into cold water. This is a very severe test, and it is difficult to find ware which will stand it. It is a fairly good comparative test and the best wares will stand the test without flying off to a great extent.

Cover Coats. Cover enamels include all those coats applied after the ground coat. These coats have two functions to perform: first, to render the ware more pleasing to the eye and thereby render it salable; second, to impart to the ware the property of resisting acids. This might be classified more properly as an essential property of the cover enamels, but still, with the thicker coating of enamel, acids are less likely to find an opening to the steel than with thinner coats, though both may be acid proof so far as their chemical composition is concerned. Hence, the writer has classified this second property as one of the functions of cover enamels, though it is certainly of minor importance as compared with the first function.

The cover coats applied vary widely as to number and qualities. In marbleized ware the cover enamels are usually white, having some colored enamel sprinkled on while the second coat of white is still wet. The operation is sometimes reversed, having the cover enamel dark and sprinkling it with white.

The cover enamels must fuse at a point below the fusing temperature of the ground coat, but their fusing temperature must not be so low as to leave the ground coat hard, because the bond between the two will be very

poor and the cover enamel may pull off from the ground coat.

Since enamel wares, especially those used for cooking purposes, are constantly in contact with acids, it is evident that the enamels must be acid proof and contain no material that can be taken out by such acids. If lead is used at all in the enamels it must be in small quantities and its combination must be so thorough that it can not be taken out with strong acetic acid. It is best to use no lead at all since one can easily get along without it.

The test applied to these coats is to boil acetic acid in the vessel. If the enamel has been attacked by the acid it will have lost its gloss where the acid was in contact with it.

THE INVESTIGATION.

The investigation here described was designed to determine the limits within which the ingredients of enamels may vary and still produce good commercial enamels. Since the ground coat is the vital part of enamel ware, the investigation was confined largely to this coat, although the cover enamels were investigated to some extent. It was necessary first to determine what constitutes a good commercial enamel. It was decided that it must have the following properties:

1. It must adhere to the steel well, therefore it must fit the steel, showing no crazing or shivering.

2. The relation between the heat treatment required by the ground coat and the subsequent coats must be such as to form a good bond between the enamels without the under coat boiling or fusing sufficiently to cause defects in the outer coat.

3. The enamel must resist the action of dilute acetic acid.

4. It must contain no lead.

5. The finished ware must present a pleasing appearance to the eye.

6. The enamel must be cheap enough to permit its use with profit to the manufacturer.

MATERIALS USED.

In order to make the investigation as thoroughly practical as possible, it was thought advisable to use the same grade of materials as are used commercially. The steel and chemicals used were accordingly obtained from the West Lafayette Manufacturing Company, which is engaged in the production of enamel ware. The steel was No. 28 gauge Bessemer steel obtained in sheets 11 inches square. The chemicals used for the production of the enamels were taken directly from the bins of the company and hence are the same as the company used for their enamels. No analysis of these materials was made, but they were all of a good commercial brand. In calculating the batch weight of the enamels, all of the chemicals were assumed to be pure, except the clay and feldspar. The formulae and combining weight assumed for these were the same as those given in the Manual of Calculation of the American Ceramic Society, as being about the average of commercial grades of these materials. The acid used in pickling was hydrochloric, which was obtained C. P. and diluted to about 5%. This is stronger than is used commercially but this is a matter of choice to a certain extent.

PREPARATION OF TEST PIECES.

The steel was cut into strips about 1 inch x 3 inches which were then bent into the form of a V. This shape of test pieces was selected because it provided an angle such as is found in commercial ware and because such pieces are convenient to handle. Each strip was marked near the end with a letter and a number designating the enamel to be applied to the strip, the mark being stamped in with steel letters. Six pieces were prepared for each enamel.

Scaling.

These test pieces were scaled by heating to dull redness in a muffle. As stated before, this is done to burn off any grease adhering to the steel and to more thoroughly oxidize the semi-oxidized surface and thereby render the pickling more rapid and thorough.

Pickling.

After scaling and cooling the test pieces were placed in dilute hydrochloric acid (about 5%) and left until the iron scale was removed. They were now taken from the acid and the bright, clean steel thoroughly washed in clean water. From here they were transferred to a bath of boiling water containing a little sodium carbonate. It is not necessary to leave them in the alkali bath only long enough to become thoroughly wetted with the solution. They were then dried on a hot plate and left in a dry place until ready for use.

The drying of the steel after the alkali bath is an important process, as is also the strength of the alkali bath. If the solution is too strong, the dried steel will have a coating of Na_2CO_3 over the surface, which is objectionable. The solution should be thoroughly alkaline but not strong enough to leave a perceptible white coating on the steel. The drying is more important still. If the steel dries too slowly it is sure to rust, and if dried too rapidly it is sure to rust. If the steel becomes too hot while drying, possibly some CO_2 will be driven out of the $NaCO_3$ and this with the water gives ideal conditions for rusting of iron. There is also a possibility that some CO_2 is driven out of the Na_2CO_3 when dissolved and especially is this possible when the solution is boiled, hence we may have the CO_2 radical in the solution. Considering these facts, the writer believes that Na_2CO_3 is not the proper reagent for this purpose, and would suggest that NaOH or KOH would be much better. In these experiments the steel was all rusted to some extent and in practice it is very seldom that the steel is free from rust when dipped and it is believed

that this condition could be improved by changing the alkali bath.

PREPARING THE ENAMELS.

The enamel batches were weighed on a balance sensible to one-tenth of a gram. After weighing they were thoroughly ground in a porcelain mortar to insure thorough mixing of the materials before fritting.

Fritting.

The fritting was done in the gas frit kiln of the ceramic department, using natural gas and compressed air at eighty pounds pressure. The temperature which can be gotten in this kiln is above cone 20 but no such temperature as this was needed for our purpose. The enamels were fritted in No. 6 Hessian crucible, four of which would just fit nicely in the furnace, hence four enamels were fritted at a time. The time and temperature of fritting were of course variable, depending on the nature of the enamel and the condition of the furnace, whether hot or cold, when the enamel was put into it. The time required, when the furnace was hot when the enamel was put into it, was usually about one hour. The temperature was not measured regularly, but it was usually about 1000° to 1200°. To determine when fritting was complete, a small iron rod was dipped into the molten glass and, being withdrawn, it drew a string of glass after it. The fritting was continued until the string was smooth, no lumps being felt when the string was drawn between the fingers. Usually it was quite easy to tell when the fritting was complete, the liquid being clear and free from bubbles and lumps of undissolved material. When the fritting was complete the crucible was drawn from the furnace, and the molten glass poured into cold water. A new charge was put into the crucible and it was immediately returned to the furnace.

Grinding.

The shattered glass was taken from the water and thoroughly dried. It was then accurately weighed and

the required per cent of raw ingredients added to it. The enamel was now wet-ground in a porcelain ball mill until it passed a 150 mesh screen and kept in Mason jars until required for use. The time required for grinding was usually about one hour.

APPLYING THE ENAMELS.

The enamel slip was poured from the Mason jar into a deep dish of convenient shape for dipping. If it was too thick, a little water was added to it. If it was too thin, a little of a solution of $MgSO_4$ was added to it. This increases the viscosity of the liquid and floats the enamel immediately, a very few drops of the solution making a great change in the consistency of the liquid. The test pieces prepared and marked for the given enamel were now dipped into it and shaken so as to secure an even coating over the piece. After dipping, the test pieces were placed in the drier immediately, in order to prevent rusting before drying.

BURNING.

Because of the varying composition of these enamels, it was evident that the heat treatment required to burn them properly would vary greatly, and although it was decided to follow commercial practice and vary the time of burning, keeping the temperature as nearly constant as possible, still it was evident that it would be necessary to vary the temperature to some extent.

The problem of getting a kiln in which the temperature could be varied rapidly was somewhat perplexing. The large muffle kilns of the department of ceramics were not at all suitable for this purpose. It was finally decided to fit a muffle in the gas frit kiln. Two bricks were taken out of the side of the kiln to provide a door for getting the ware in and out, and a sagger 9 inches square was fitted into the kiln for a muffle. This provided a very satisfactory arrangement, as it was plenty large enough

for our purpose and the temperature could be raised or lowered with great rapidity and ease. There were no data available to show what temperatures are actually used in practice, but from observations taken it was decided that the temperature probably varied between 800°C and 1000°C. The temperature of the furnace was measured with a LeChatelier pyrometer. The furnace was heated to 1040°C and those enamels which had been selected as being the most refractory were tried at this temperature. Having six test pieces for each enamel, it was possible to find the treatment which would give favorable results before exhausting them.

The time required for burning was considerably less than is used in practice, the reason for this being that the temperature of the furnace was not materially affected by putting one of these small test pieces into it, and the test piece rapidly assumed the temperature of the furnace. In practice the amount of ware put into the furnace at one time is so large that the furnace is chilled considerably when charged, and about half of the time required for burning is consumed in the ware assuming the temperature of the furnace.

Although it is the general practice in burning enamels to vary the time to suit the temperature, it is bad practice and if followed beyond a limited degree, results in bad ware.

Every enamel formula has a definite temperature, varying within quite narrow limits, at which it should be burned to give good results, and if this temperature is varied outside of these limits, the result will be bad ware.

The time of burning may be varied to suit the thickness of the coat, but the temperature should be kept constant.

GROUND COAT DATA.

As stated before, the investigation was confined largely to the ground coat, because of its greater import-

ance in the enamel field. The first requisite in outlining the investigation was to obtain a formula suitable as a basis for the work. There was available a number of formulae which are used commercially, but it was not known which of these were good or which were bad or whether they represented the means or the extremes in the field of allowable composition. We desired as a basis for the work a formula which would represent the mean in the field of allowable composition, and selected the average of these formulae as a basis for the work. This was still more or less of a guess, but the results will show that the selection was well made.

Having selected a formula as a basis for the work, the ingredients entering the formula were varied as far as thought necessary in order to reach a limit. It will be noticed that the sum of R. O. elements is kept equal to 1 in all series. In order to do this it was sometimes necessary to vary one element at the expense of another, but where possible, only one element was varied at a time.

The formulae from which the basis for the work was selected were as follows:

No.	K_2O	Na_2O	CaO	CoO	MnO_2	Al_2O_3	SiO_2	B_2O_3
1	.155	.602	.233	.006	.003	.169	1.7	.562
2	.152	.617	.226	.003	.002	.185	1.1	.350
3	.166	.475	.344	.008	.000	.191	1.64	.306
4	.161	.477	.268	.062	.028	.210	1.72	.303
5	.157	.672	.160	.009	.000	.210	1.58	.427
Average	.15	.60	.24	.006	.004	.20	1.5	.40

The materials used were as follows:

Name	Formula	Equivalent Weight
Clay	.86 K_2O Al_2O_3 2.1 (SiO_2) 2.2 (H_2O)	267
Feldspar	.14 Na_2O 1.1 Al_2O_3 6.6 SiO_2	600
Borax	Na_2O 2 B_2O_3 10 (H_2O)	382
Boric acid	B_2O_3 3 (H_2O)	124
Fluorspar	CaF_2	78
Whiting	$CaCO_3$	100
Flint	SiO_2	60
Manganese Oxide	MnO_2	87
Salt Petre	KNO_3	202
Soda Ash	Na_2CO_3	106
Cryolite	Na_3AlF_6	420
Black Oxide Cobalt	Co_2O_4	80

SERIES A.

No.	K_2O	Na_2O	CaO	CoO	MnO_2	Al_2O_3	SiO_2	B_2O_3
1	1.5	.60	.24	.006	.004	.20	.80	.40
2	1.5	.60	.24	.006	.004	.20	.90	.40
3	1.5	.60	.24	.006	.004	.20	1.10	.40
4	1.5	.60	.24	.006	.004	.20	1.30	.40
5	1.5	.60	.24	.006	.004	.20	1.50	.40
6	1.5	.60	.24	.006	.004	.20	1.70	.40
7	1.5	.60	.24	.006	.004	.20	1.90	.40
8	1.5	.60	.24	.006	.004	.20	2.10	.40

BATCH FORMULAE.

No.	Spar	Flint	Borax	Soda	KNO_3	Fl'spr	Cry'lte	Cobalt	MnO_2
1	.1	.07	.19	.22	.06	.24	.06	.006	.004
2	.1	.17	.19	.22	.06	.24	.06	.006	.004
3	.1	.37	.19	.22	.06	.24	.06	.006	.004
4	.1	.57	.19	.22	.06	.24	.06	.006	.004
5	.1	.77	.19	.22	.06	.24	.06	.006	.004
6	.1	.97	.19	.22	.06	.24	.06	.006	.004
7	.1	1.17	.19	.22	.06	.24	.06	.006	.004
8	.1	1.37	.19	.22	.06	.24	.06	.006	.004

In this series, as well as all of the following, there was added raw, 5% clay and 2% boiled borax. The borax was boiled for a short time and added to the enamel in the mill. The object of the raw clay is to float the enamel. The borax tempers the enamel, producing what is called shortness. This property prevents the enamel slip from flowing down the sides of the ware after dipping. $MgSO_4$ produces the same results, but when used in the ground coat it causes the steel to rust before drying. The percentage given represents per cent of the fritted weight of the material.

RESULTS OF THE SERIES.

Number 1. Very poor. Crazes badly. Adheres poorly. Burns off easily.

Number 2. Poor. Adheres poorly. Crazes badly.

Number 3. Crazes very slightly. Adheres fairly well.

Number 4. Good enamel. Adheres well.

Number 5. Good enamel. Adheres well.

Number 6. Good enamel. Adheres well.

Number 7. Shivers to some extent. Adheres rather poorly.

Number 8. Poor enamel. Shivers badly. Adheres very poorly.

This series shows the effect of SiO_2 in enamels to be the same as in glazes. Low SiO_2 causes crazing. High SiO_2 causes shivering. The allowable limits of SiO_2, according to these results, are 1.1 SiO_2 to 1.7 SiO_2.

Numbers 7 and 8, being the most refractory enamels in this series, were both underburned. The fact that these enamels shivered when underburned is an indication that their coefficient of expansion is higher than that of the steel, but the fact remains that there are a great many good commercial enamels which will shiver when underburnt, therefore, it is possible that both of these enamels would have been good had they been well burnt, thereby producing a good bond between the enamel and the steel.

There is no doubt but that numbers 4 and 5 are better enamels than 7 or 8, but since the latter were underburnt, the data is unreliable, therefore the upper limit given can not be accepted as having any value. The series certainly proves, however, that high SiO_2 causes shivering and low SiO_2 causes crazing.

SERIES B.

No.	K_2O	Na_2O	CaO	CoO	MnO_2	Al_2O_3	SiO_2	B_2O_3
1	.15	.60	.24	.006	.004	.20	1.50	.0
2	.15	.60	.24	.006	.004	.20	1.50	.1
3	.15	.60	.24	.006	.004	.20	1.50	.2
4	.15	.60	.24	.006	.004	.20	1.50	.3
5	.15	.60	.24	.006	.004	.20	1.50	.4
6	.15	.60	.24	.006	.004	.20	1.50	.5
7	.15	.60	.24	.006	.004	.20	1.50	.6
8	.15	.60	.24	.006	.004	.20	1.50	.7

BATCH FORMULAE.

No.	Spar	Flint	Borax	Soda	KNO_3	Fl'spr	Cry'lte	Cobalt	MnO_2
1	.1	.77	0	.42	.06	.24	.05	.006	.004
2	.1	.77	.04	.37	.06	.24	.05	.006	.004
3	.1	.77	.09	.32	.06	.24	.05	.006	.004
4	.1	.77	.14	.27	.06	.24	.05	.006	.004
5	.1	.77	.19	.22	.06	.24	.05	.006	.004
6	.1	.77	.24	.17	.06	.24	.05	.006	.004
7	.1	.77	.29	.12	.06	.24	.05	.006	.004
8	.1	.77	.34	.07	.06	.24	.05	.006	.004

RESULTS.

Number 1. Very matt. Badly pinholed. Poor.

Number 2. Poor. Very matt. Slightly better than No. 1.

Number 3. Fair. Has a little gloss. Slightly pinholed.

Number 4. Fair gloss. Adheres fairly well. Fair enamel.

Number 5. Original formula. (See A-5 or C-3.)

Number 6. Good gloss. Shivers badly. Adheres well.

Number 7. Fine gloss. Shivers badly. Adheres poorly.

Number 8. Elegant gloss. Shivers very badly. Adheres poorly.

This series shows that boracic acid is highly efficient in bringing a desirable polish on the ware. It also shows that B_2O_3 acts the same as SiO_2 with respect to the coefficient of expansion of the enamel and it is a stronger agent in producing shivering than SiO_2. The allowable limits of B_2O_3 in this formula are .2 to .5 B_2O_3.

SERIES C.

No.	K_2O	Na_2O	CaO	CoO	MnO_2	Al_2O_3	SiO_2	B_2O_3
1	.15	.60	.24	.006	.004	.10	1.5	.40
2	.15	.60	.24	.006	.004	.20	1.5	.40
3	.15	.60	.24	.006	.004	.30	1.5	.40
4	.15	.60	.24	.006	.004	.40	1.5	.40
5	.15	.60	.24	.006	.004	.50	1.5	.40

BATCH FORMULAE.

No.	Spar	Flint	Borax	Soda	KNO_3	Fl'spr	Cry'lte	Cobalt	MnO_2
1	.1	1.43	.19	.23	.15	.24	.056	.006	.004
2	.1	.77	.19	.22	.06	.24	.056	.006	.004
3	.1	.56	.19	.22	.06	.24	.056	.006	.004
4	.1	.35	.19	.22	.06	.24	.056	.006	.004
5	.1	.14	.19	.22	.06	.24	.056	.006	.004

RESULTS.

Number 1. Shivers slightly, adheres poorly.

Number 2. Good enamel. Adheres tenaceously, fine gloss.

Number 3. Good enamel. Adheres tenaceously, fine gloss.

Number 4. Good enamel. Adheres tenaceously, fine gloss.

Number 5. Good enamel. Adheres tenaceously, fine gloss.

This series shows that clay substance is desirable for good results—the upper limit was not reached.

SERIES D.

No.	K_2O	Na_2O	CaO	CoO	MnO_2	Al_2O_3	SiO_2	B_2O_3
1	.15	.61	.24	.00	.004	.20	1.5	.40
2	.15	.60	.24	.01	.004	.20	1.5	.40
3	.15	.59	.24	.02	.004	.20	1.5	.40
4	.15	.58	.24	.03	.004	.20	1.5	.40
5	.15	.57	.24	.04	.004	.20	1.5	.40
6	.15	.56	.24	.05	.004	.20	1.5	.40
7	.15	.55	.24	.06	.004	.20	1.5	.40

BATCH FORMULAE.

No.	Spar	Flint	Borax	Soda	KNO_3	Fl'spr	Cry'lte	Cobalt	MnO_2
1	.1	.77	.19	.23	.06	.24	.05	0	.004
2	.1	.77	.19	.22	.06	.24	.05	.01	.004
3	.1	.77	.19	.21	.06	.24	.05	.02	.004
4	.1	.77	.19	.20	.06	.24	.05	.03	.004
5	.1	.77	.19	.19	.06	.24	.05	.04	.004
6	.1	.77	.19	.18	.06	.24	.05	.05	.004
7	.1	.77	.19	.17	.06	.24	.05	.06	.004

RESULTS.

Number 1. Adheres poorly. Not a good enamel.

The entire series except Number 1 shows good results. The increase in cobalt does not show a corresponding in-

crease in the quality of the ware, but the series demonstrates very clearly that a little cobalt is desirable in producing a good tough enamel. The cobalt increases the stability of the enamel in burning and gives it a wider range of fusion than the same enamel without cobalt. The limit is defined by the cost of the enamel and .06 cobalt makes the enamel too expensive.

SERIES E.

No.	K_2O	Na_2O	CaO	CoO	MnO_2	Al_2O_3	SiO_2	B_2O_3
1	.15	.84	.00	.006	.004	.20	1.50	.40
2	.15	.70	.14	.006	.004	.20	1.50	.40
3	.15	.60	.24	.006	.004	.20	1.50	.40
4	.15	.50	.34	.006	.004	.20	1.50	.40
5	.15	.40	.44	.006	.004	.20	1.50	.40
6	.15	.30	.54	.006	.004	.20	1.50	.40
7	.15	.20	.64	.006	.004	.20	1.50	.40

BATCH FORMULAE.

No.	Spar	Flint	Borax	Soda	KNO_3	Fl'spr	Cry'lte	Cobalt	MnO_2	Clay	B_2O_3, $3H_2O$
1	.1	.77	.19	.46	.06	.0	.05	.006	.004	0	0
2	.1	.77	.19	.32	.06	.14	.05	.006	.004	0	0
3	.1	.77	.19	.22	.06	.24	.05	.006	.004	0	0
4	.1	.77	.19	.12	.06	.34	.05	.006	.004	0	0
5	.1	.70	.19	.12	.06	.44	.02	.006	.004	.03	0
6	.1	.70	.09	.12	.06	.54	.02	.006	.004	.03	.20
7	.1	.70	.00	.10	.02	.64	.02	.006	.004	.03	.18

RESULTS.

Number 1. Burns off very easily. Too soft. No good results were obtained with this enamel.

Number 2. Very good enamel. Adheres well.

Number 3. Good enamel. Adheres well.

Number 4. Good enamel. Adheres well.

Number 5. Very good enamel but hard.

Number 6. Very badly pinholed. This is possibly due to the fact that this enamel was not very well fritted. It is quite refractory.

Number 7. Very refractory but good if well burnt.

This series demonstrates the fact that lime has a great influence on the refractoriness of the enamels, but it may be varied within quite wide limits. The lower limit of lime as found in this formula is .14 CaO. The upper limit is not definitely established but it certainly would not be advisable to use more than .64 CaO, as this amount makes the enamel very refractory.

SERIES F.

No.	K_2O	Na_2O	CaO	CoO	MnO_2	Al_2O_3	SiO_2	B_2O_3
1	.00	.75	.24	.006	.004	.20	1.5	.40
2	.15	.60	.24	.006	.004	.20	1.5	.40
3	.30	.45	.24	.006	.004	.20	1.5	.40
4	.45	.30	.24	.006	.004	.20	1.5	.40
5	.60	.15	.24	.006	.004	.20	1.5	.40
6	.75	.00	.24	.006	.004	.20	1.5	.40

BATCH FORMULAE.

No.	Spar	Flint	Borax	Soda	KNO_3	Fl'spr	Cry'lte	Cobalt	MnO_2	Clay	B_2O_3, $3H_2O$
1	.0	.65	.19	.37	.0	.24	.05	.006	.004	.11	0
2	.1	.77	.19	.22	.06	.24	.05	.006	.004	0	0
3	.1	.77	.19	.07	.21	.24	.05	.006	.004	0	0
4	.1	.67	.19	.07	.36	.24	.05	.006	.004	.05	0
5	.1	.67	.04	.07	.51	.24	.05	.006	.004	.05	.32
6	.1	1.02	.0	.0	.75	.24	.05	.006	.004	.19	.40

RESULTS.

This enamel was applied too thinly on the test pieces, hence during burning the steel was oxidized very rapidly, causing the black specks. It is probable that this enamel, if properly applied, is as good as any in the series.

Number 1. Very spotted with black specks of iron scale. Very soft.

Number 2. Good enamel. Adheres well.

Number 3. Good enamel. Adheres well.

Number 4. Good enamel. High gloss. Adheres well.

Number 5. Good enamel. High gloss. Adheres well.

Number 6. Good enamel. High gloss. Adheres well.

This series shows that K_2O is more effective in producing a polish on the ware than is Na_2O. It also seems to show that K_2O acts similar to CaO in making the enamel more refractory than the enamel in which all of the K_2O is replaced by Na_2O. The difference in refractoriness of these enamels was very small and it is easily possible that this apparent difference was caused by the difference in

thickness of the coat, hence it is probable that if these enamels were uniformly applied, the data obtained would bear out conclusions drawn from previous experiments, viz., that K_2O is a stronger flux than Na_2O. The lower limit of K_2O is .15, but the upper limit was not found, which seems to show that the ratio of K_2O to Na_2O is not important in enamels.

SERIES G.

No.	K_2O	Na_2O	CaO	CoO	MnO_2	Al_2O_3	SiO_2	B_2O_3
1	.15	.60	.24	.006	.004	.20	1.5	.40
2	.15	.60	.24	.006	.004	.20	1.5	.40
3	.15	.60	.24	.006	.004	.20	1.5	.40
4	.15	.60	.24	.006	.004	.20	1.5	.40
5	.15	.60	.24	.006	.004	.20	1.5	.40

BATCH FORMULAE.

No.	Spar	Flint	Borax	Soda	KNO_3	Fl'spr	Cry'lte	Cobalt	MnO_2
1	.16	.37	.19	.380	.010	.24	.00	.006	.004
2	.12	.63	.19	.384	.046	.24	.04	.006	.004
3	.08	.90	.19	.388	.082	.24	.08	.006	.004
4	.04	1.16	.19	.392	.118	.24	.12	.006	.004
5	.00	1.43	.19	.396	.154	.24	.16	.006	.004

This series was designed to determine the effect of replacing feldspar with cryolite and vice versa. It will be noted that several of the ingredients are varied in order to keep the ultimate formula constant, but none vary greatly except the feldspar and the cryolite and the flint, which was necessary in order to replace the SiO_2 of the spar.

RESULTS.

Number 1. Shivers worse than any enamel yet found. Large circular flakes chip off. Adheres very poorly.

Number 2. Similar to Number 1, but not as bad.

Number 3. Very good enamel. Adheres well.

Number 4. Very good enamel. Adheres well, but crazes very slightly. Slightly opaque.

Number 5. Crazes badly. Adheres poorly. Quite opaque. Yellowish-green color.

This series demonstrates several important facts. All spar and no cryolite results in shivering. All cryolite and no spar results in crazing. Cryolite tends to make the enamel opaque, giving a yellowish-green color. A mixture of spar and cryolite is better than either alone.

The fact that increase of cryolite causes crazing is probably due to the loss of SiO_2 from the expulsion of fluorine in the form of SiF_4.

SERIES H.

No.	K_2O	Na_2O	CaO	CoO	MnO_2	Al_2O_3	SiO_2	B_2O_3
1	.15	.60	.24	.006	.004	.20	1.5	.40
2	.15	.60	.24	.006	.004	.20	1.5	.40
3	.15	.60	.24	.006	.004	.20	1.5	.40
4	.15	.60	.24	.006	.004	.20	1.5	.40
5	.15	.60	.24	.006	.004	.20	1.5	.40

BATCH FORMULAE.

No.	Spar	Flint	Borax	Soda	KNO_3	Fl'spr	Wh'tg	Cry'	CoO	MnO_2
1	.1	.77	.19	.22	.06	.24	.00	.05	.006	.004
2	.1	.77	.19	.22	.06	.18	.06	.05	.006	.004
3	.1	.77	.19	.22	.06	.12	.12	.05	.006	.004
4	.1	.77	.19	.22	.06	.06	.18	.05	.006	.004
5	.1	.77	.19	.22	.06	.00	.24	.05	.006	.004

This series was designed to determine the effect of substituting whiting for fluorspar. The result of the series shows that there is absolutely no choice between the two reagents so far as the quality of the enamel produced is concerned. The price should be the governing factor in the selection.

BURNING DATA.

SERIES A.

No.	Temperature.	Time.
1	1030°C	30—40 seconds
2	1030°C	30—40 seconds
3	1030°C	30—40 seconds
4	1030°C	30—45 seconds
5	1040°C	40—50 seconds
6	1040°C	40—50 seconds
7	1040°C	1 min. to 1 min. 20 sec.
8	1040°C	1 min. to 1 min. 40 sec.

SERIES B.

No.	Temperature.	Time.
1	1010°C	30—60 seconds
2	1010°C	50—60 seconds
3	1000°C	40—50 seconds
4	1000°C	40—55 seconds
5	.....	.....
6	1000°C	50—1 min. 15 sec.
7	1000°C	50—60 seconds
8	1000°C	40—1 min. 10 sec.

SERIES C.

1	1000°C	35—40 seconds
2	1010°C	30—40 seconds
3	1010°C	35—50 seconds
4	1000°C	50—60 seconds
5	1000°C	50—60 seconds

SERIES D.

1	1010°C	30—40 seconds
2	1010°C	30—40 seconds
3	1010°C	30—40 seconds
4	1010°C	30—50 seconds
5	1010°C	25—40 seconds
6	1010°C	25—40 seconds
7	1010°C	25—40 seconds

SERIES E.

No.	Temperature.	Time.
1	1000°C	Over-burnt in 15 seconds
2	1000°C	30—40 seconds
3	.....	.....
4	1000°C	40—60 seconds
5	1000°C	30—50 seconds
6	1000°C	40—50 seconds
7	1000°C	40—50 seconds

SERIES F.

1	1000°C	40—50 seconds
2 original	.....	.....
3	1000°C	25—35 seconds
4	1000°C	40—50 seconds
5	1000°C	30—50 seconds
6	1000°C	50—60 seconds

SERIES G.

1	1000°C	50—60 seconds
2	1000°C	40—50 seconds
3	1000°C	25—35 seconds
4	1000°C	30—40 seconds
5	1000°C	30—50 seconds

SERIES H.

No.	Temperature	Time
1	.....	.....
2	1000°C	50—60 seconds
3	1000°C	40—50 seconds
4	1000°C	45—1 min. 20 sec.
5	1000°C	40—50 seconds

NOTES ON THE DATA.

The burning data represents the treatment given only those test pieces which were worthy of consideration. It must be understood, however, that this work was purely experimental, there being no data available to show what temperature is actually used in practice, and therefore this treatment might be the best and it might not. It is a well known fact that the time and temperature are varied quite widely in practice. In fact, the only method of measuring the temperature of the furnace in practice is very often by the use of the eye which is very inaccurate, but the burners vary the time to suit the temperature.

It must also be remembered that the thickness of the enamel coat has a very marked effect on the time required for burning, and since this factor is liable to vary greatly in applying so many different enamels, it is likely to make some of the data appear inconsistent. There are a few seeming inconsistencies in this data which can only be explained from this cause.

DEFECTS OF THE WARE.

As will be noted from the description of the results, the defects produced in this ware are very closely allied to the defects in glazes. The burning of enamel ware is a process requiring skill to be properly executed, and in the hands of the inexperienced it is quite possible that poor results be produced with a good enamel.

Overburning and underburning produce very similar results so far as the appearance of the ware is concerned and it is very often difficult to tell whether a piece of ware is overburnt or underburnt. The overburnt ware is pimpled very badly, but if the degree of overburning is excessive, the iron will be oxidized enough to come through the enamel and the ware will present the appearance of steel just taken from the scaling furnace.

Underburning very seldom produces the appearance of steel covered with iron scale, but it does produce the pimpled ware the same as overburning.

When the ware comes from the furnace black and covered with iron scale, burners often say it is burnt off, but the fact is that the iron is so heavily oxidized that the scale has combined largely with the enamel and completely covered it.

One great defect of enamels is to fly off of the steel, either entirely or in patches. This may occur in the furnace, or while the ware is cooling, or any time after it is cool. The defect is usually inherent in the enamel, but the same defect will occur in some good enamels if they are not thoroughly dry when put into the furnace or if underburnt.

This defect was found in a very moderate form in some of the ware produced in this investigation. It appears here in light colored spots, varying in size from the size of a pin head to one-fourth of an inch in diameter. These are spots where the enamel is loose from the steel and in some cases small chips flew out of the spots, leaving the steel exposed. What the cause of this defect is has not been definitely determined. The cause is the same, whether the enamel flies off of the steel entirely or only pulls loose in spots, and to the writer there seems but one explanation for it and that is the difference in the coefficient of expansion of the steel and the enamel. Those enamels which showed this defect had compositions which, in glazes, would tend toward shivering, but the way in

which this defect presents itself is entirely different from the way in which shivering presents itself.

When the enamel flies off of the steel in the fire, it is probably due to the fact that the vitrified enamel can not expand as much as the steel and hence pulls loose. If the enamel is not dry when put into the furnace, the steel heats up more rapidly than the enamel and this causes the enamel to pull loose from the steel. It will be noted that the above described defect has been called shivering. Although evidence points to the fact that it is shivering, still it has not been proven to be such, and hence too much importance must not be attached to that statement.

Crazing presents itself in enamels in the same way as in glazes and the composition necessary to produce it is the same as in glazes.

CONCLUSIONS.

Discussing the different elements in the enamels, the following conclusions are drawn as to their effect on the enamel and their allowable limits of variation.

Na_2O and K_2O may be interchanged to any desired extent without making any marked changes in the results. The most perceptible change is in the brilliance of the enamels. Increase of K_2O increases the brilliance of the enamel.

CaO.

The replacement of K_2O with CaO hardens the enamel very markedly. An enamel containing no CaO is entirely too soft for any practical value. The allowable limits of CaO are .14 equivalent to .64 equivalent.

CoO.

This element increases the stability of the enamel in burning and the toughness of the resulting enamel. It also intensifies the whiteness of a white enamel applied over the ground coat. Although not absolutely essential to produce a good ground coat, it is desirable. The allowable limit is established only by the cost, and .06 equiva-

lent is as much as can possibly be profitably used in ordinary commercial ware.

Al_2O_3.

Increase of Al_2O_3 increases the brilliance and adhesiveness of the glaze up to .5 equivalent. It increases the refractoriness of the enamel, rendering fritting very difficult, and increases the viscosity, so that the molten enamel will hardly run out of the crucible.

The limits established are .1 equivalent and .5 equivalent.

SiO_2.

High SiO_2 causes shivering. Low SiO_2 causes crazing. Increase of SiO_2 hardens the enamel. The lower limit established is 1.1 equivalent.

B_2O_3.

High B_2O_3 causes shivering. Low B_2O_3 produces matt enamels. B_2O_3 is a stronger agent in producing shivering than SiO_2. It is also a stronger agent in affecting the brilliance of the enamel than SiO_2. The limits established are .2 equivalent and .5 equivalent.

CaF_2 vs. $CaCO_3$.

The substitution of $CaCO_3$ for CaF_2 produces no change in the quality of the ware produced, but it hardens the raw enamel a little, making it more difficult to frit. The substitution may be made to any desired extent without any appreciable change in the results.

Cryolite vs. Feldspar.

Substitution of cryolite for feldspar softens the enamel very markedly and produces opacity. High cryolite and low feldspar causes crazing. High feldspar and low cryolite cause shivering. The best results were obtained with mixtures of equal amounts of the two.

It must be remembered that these conclusions can only be strictly applied to this one particular formula which was used for the basis of this work. The limits are so sharply defined, however, that valuable deduction can certainly be made from these results with regard to the

relation which should exist between the ingredients of enamels.

COVER ENAMELS.

All of the work done on cover enamels was confined to white coats. The preparation of the enamels was precisely the same as the preparation of the ground coat enamels. These enamels were applied to the best ground coats obtained in the previous experiments.

The basis for this work was obtained in the same way as that for the ground coat work. Having at hand a number of formulae which are used commercially, five of these formulae were selected representing the extremes in the field of composition, and the average of these was taken as a basis for the investigation.

The materials used were the same as those used in the ground coat except the opacifying agents. The formulae from which the basis for the work was selected are as follows:

No.	K_2O	Na_2O	CaO	Al_2O_3	SiO_2	B_2O_3
1	.234	.437	.327	.153	1.70	.33
2	.211	.391	.396	.154	1.60	.34
3	.164	.450	.382	.104	1.40	.42
4	.126	.534	.342	.100	1.53	.19
5	.189	.567	.243	.149	1.78	.35
Av.	.150	.500	.350	.100	1.60	.30

Each of these formulae calls for 10% SnO_2 and 2% clay, calculated in per cent of the fritted weight. Hence the formula used as the basis for the work is as follows:

$$\left.\begin{matrix} .15\ K_2O \\ .50\ Na_2O \\ .35\ CaO \end{matrix}\right\} .1\ Al_2O_3 \left\{\begin{matrix} 1.6\ SiO_2 \\ .3\ B_2O_3 \end{matrix}\right.$$

add raw: 10% SnO_2 plus 2% clay.

The SnO_2 and clay are not given in the ultimate formulae which follow but they are given in equivalents in the batch formulae.

SERIES A.

No.	K_2O	Na_2O	CaO	Al_2O_3	SiO_2	B_2O_3
1	.15	.5	.35	.10	1.0	.30
2	.15	.5	.35	.10	1.2	.30
3	.15	.5	.35	.10	1.4	.30
4	.15	.5	.35	.10	1.6	.30
5	.15	.5	.35	.10	1.8	.30

BATCH FORMULAE.

No.	Spar	Flint	Borax	Soda	KNO_3	CaF_2	SnO_2	Clay
1	.091	.4	.15	.34	.07	.35	.13	.014
2	.091	.6	.15	.34	.07	.35	.13	.014
3	.091	.8	.15	.34	.07	.35	.13	.014
4	.091	1.0	.15	.34	.07	.35	.13	.014
5	.091	1.2	.15	.34	.07	.35	.13	.014

RESULTS.

Number 1. Too soft. Not very white. Dull lustre.
Number 2. Fair white. More brilliant than No. 1.
Number 3. Good white. Brilliant enamel.
Number 4. Good white. Brilliant enamel.
Number 5. Good but a little too hard.

SERIES B.

No.	K_2O	Na_2O	CaO	Al_2O_3	SiO_2	B_2O_3
1.	.15	.5	.35	.10	1.6	.00
2	.15	.5	.35	.10	1.6	.10
3	.15	.5	.35	.10	1.6	.20
4	.15	.5	.35	.10	1.6	.30
5	.15	.5	.35	.10	1.6	.40
6	.15	.5	.35	.10	1.6	.50

BATCH FORMULAE.

No.	Spar	Flint	Borax	Soda	KNO_3	CaF_2	SnO_2	Clay
1	.091	1.0	0	.64	.07	.35	.13	.014
2	.091	1.0	.05	.54	.07	.35	.13	.014
3	.091	1.0	.10	.44	.07	.35	.13	.014
4	.091	1.0	.15	.34	.07	.35	.13	.014
5	.091	1.0	.20	.24	.07	.35	.13	.014
6	.091	1.0	.25	.14	.07	.35	.13	.014

RESULTS.

Number 1. Too hard. No gloss, not very white.

Number 2. Too hard. Poor gloss, more opaque than No. 1.

Number 3. Very nice. Good gloss.

Number 4. Very nice. Fine gloss.

Number 5. Very nice, brilliant enamel.

SERIES C.

No.	K_2O	NaO	CaO	Al_2O_3	SiO_2	B_2O_3
1	.15	.5	.35	.0	1.6	.30
2	.15	.5	.35	.1	1.6	.30
3	.15	.5	.35	.2	1.6	.30
4	.15	.5	.35	.3	1.6	.30
5	.15	.5	.35	.4	1.6	.30

BATCH FORMULAE.

No.	Spar	Flint	Borax	Soda	KNO_3	CaF_2	Clay	SnO_2	Raw Clay
1	.0	1.60	.15	.35	.15	.35	0	.13	.014
2	.091	1.00	.15	.35	.07	.35	0	.13	.014
3	.091	.79	.15	.35	.07	.35	.1	.13	.014
4	.091	.58	.15	.35	.07	.35	.2	.13	.014
5	.091	.37	.15	.35	.07	.35	.3	.13	.014

RESULTS.

Number 1. Burns off rather easily but good if well burnt.

Number 2. Very nice, white enamel.

Number 3. Very nice, brilliant enamel.

Number 4. Very nice, elegant gloss, very white.

Number 5. Very nice, elegant gloss, very white. But tends to crawl slightly. Quite refractory.

SERIES D.

No.	K_2O	Na_2O	CaO	Al_2O_3	SiO_2	B_2O_3
1	.15	.84	.0	.1	1.6	.30
2	.15	.64	.2	.1	1.6	.30
3	.15	.44	.4	.1	1.6	.30
4	.15	.24	.6	.1	1.6	.30

BATCH FORMULAE.

No.	Spar	Flint	Borax	Soda	KNO_3	CaF_2	SnO_2	Clay
1	.091	1	.15	.68	.07	0	.13	.014
2	.091	1	.15	.48	.07	.2	.13	.014
3	.091	1	.15	.28	.07	.4	.13	.014
4	.091	1	.15	.08	.07	.6	.13	.014

RESULTS.

Number 1. Too soft. This enamel burned to a solid gloss at a temperature less than 200°C.

Number 2. Quite soft. Fair white enamel.

Number 3. Very nice, white enamel.

Number 4. Quite hard but is good on a hard ground coat.

SERIES E.

No.	K_2O	Na_2O	CaO	Al_2O_3	SiO_2	B_2O_3	SnO_2	Raw Clay
1	0	.65	.35	.10	1.6	.30	.13	.014
2	.15	.50	.35	.10	1.6	.30	.13	.014
3	.30	.35	.35	.10	1.6	.30	.13	.014
4	.45	.20	.35	.10	1.6	.30	.13	.014
5	.60	.05	.35	.10	1.6	.30	.13	.014

BATCH FORMULAE.

No.	Spar	Flint	Borax	Soda	KNO_3	CaF_2	Cry'	B_2O_3 $3H_2O$
1	.000	1.6	.15	.20	.00	.35	.1	0
2	.091	1.0	.15	.34	.07	.35	0	0
3	.091	1.0	.15	.19	.22	.35	0	0
4	.091	1.0	.15	.04	.37	.35	0	0
5	.091	1.0	.15	.04	.52	.35	0	.30

RESULTS.

Every formula in this series produces a very nice white enamel.

SERIES F.

No.	K_2O	Na_2O	CaO	Zno	Al_2O_3	Sb_2O_3	SiO_2	B_2O_3
1	.15	.50	.35	0	.10	0	1.6	.30
2	.15	.46	.35	.02	.10	.02	1.6	.30
3	.15	.42	.35	.04	.10	.04	1.6	.30
4	.15	.38	.35	.06	.10	.06	1.6	.30

BATCH FORMULAE.

No.	Spar	Flint	Borax	Soda	KNO_3	CaF_2	ZnO	Sb_2O_3	SnO_2	Clay
1	.091	1.0	.15	.34	.07	.35	0	0	.13	.014
2	.091	1.0	.15	.30	.07	.35	.02	.02	.09	.014
3	.091	1.0	.15	.26	.07	.35	.04	.04	.05	.014
4	.091	1.0	.15	.22	.07	.35	.06	.06	.01	.014

This series was designed to determine the effect produced by replacing SnO_2 with ZnO and Sb_2O_3. The SnO_2 was added raw as in all previous formulae but the ZnO and Sb_2O_3 were fritted.

RESULTS.

The result of the series shows that the substitution can be made with good results. The best white enamel produced was Number 3 in this series.

BURNING DATA.

SERIES A.

No.	Temperature.	Time.
1	925°C	40—50 seconds
2	925°C	45—50 seconds
3	900°C	50—65 seconds
4	870°C	1 min. 20 sec.—1 min. 50 sec.
5	870°C	1 min. 30 sec.—2 min. 0 sec.

SERIES B.

1	870°C	1 min. 30 sec.—2 min. 0 sec.
2	850°C	50 sec.—65 sec.
3	850°C	50 sec.—1 min. 10 sec.
4	.....	.....
5	850°C	1 min. 10 sec.— 2 min. 0 sec.
6	850°C	60 sec.—1 min. 30 sec.

SERIES C.

No.	Temperature.	Time
1	870°C	40 sec.—60 sec.
2	.....	.....
3	900°C	1 min.—1 min. 20 sec.
4	900°C	1 min.—1 min. 20 sec.
5	925°C	1 min.—1 min. 50 sec.

SERIES D.

1	925°C	Overburnt in 10 seconds.
2	900°C	30 sec.—40 sec.
3	900°C	40 sec.—1 min.
4	900°C	50 sec.—70 sec.

SERIES E.

1	900°C	50 sec.—1 min.
2	.....	.....
3	900°C	50 sec.—1 min. 10 sec.
4	925°C	40 sec.—1 min.
5	925°C	50 sec.—1 min. 10 sec.

SERIES F.

1	.....	.....
2	925°C	50 sec.—1 min.
3	925°C	50 sec.—1 min. 5 sec.
4	925°C	50 sec.—1 min. 5 sec.

NOTES ON THE DATA.

A comparison of the burning data on the ground coat enamels and the cover enamels will show that the temperature of burning the cover enamels was lower than that of the ground coats, but the time required to burn the cover enamels was usually longer than that of burning the ground coats.

This burning data has very little value except as connected with this particular piece of work, showing the treatment necessary to mature these enamels on these small test pieces and under the condition described.

It must be borne in mind that these same enamels would require entirely different treatment if applied on commercial ware and burned under commercial conditions, and even then, the same enamel will require entirely different heat treatment depending on the fineness of grinding, degree of fritting, thickness of application and various other factors.

CONCLUSIONS.

The one general conclusion that can be drawn from the results is, that it is a very easy matter to produce a good white enamel, if it is applied on a good, hard ground coat.

These enamels were all applied on a good, hard ground coat and hence very few of them were found to be too hard. The results, however, are only comparative, and several of these enamels would prove too hard if the ground coat was not quite refractory.

The work on the cover enamels is defective in some cases, in that the variation was not wide enough to reach the limit, but still the variations are wide enough to establish a wide field of good enamels.

The following conclusions are drawn as to the effect of the different elements in the cover enamels.

K_2O vs Na_2O.

These elements may be exchanged, one for the other without any appreciable change in the result, except that K_2O produces brighter glass than Na_2O.

CaO.

This element is the most active element in the enamel in affecting the refractoriness of the enamel. Enamels in which all CaO is replaced by Na_2O are entirely too soft for any practical use. The CaO must not be reduced below .2 for good results.

Al_2O_3.

Increase of this element, increases the opacity and brilliancy of enamels and makes them harder. Good results can be obtained in the absence of this element but it is a desirable element in the enamels. It may be used in amounts varying from 0 to .4 equivalent with excellent results.

SiO_2.

Increase of SiO_2 hardens the enamel and insures safety against acids. Decrease of SiO_2 softens the enamel, decreases its brilliance and increases danger of its solution by acids. The limits established are 1.0 equivalent to 1.8 equivalent.

B_2O_3.

Increase of B_2O_3 softens the enamel and increases its lustre. Decrease of B_2O_3 has the reverse effect on the enamel. The allowable limit to which it may be decreased is .2 equivalent B_2O_3. The upper limit was not reached.

SnO_2 vs. $ZnO+Sb_2O_3$.

SnO_2 produces opacity alone, but it may be either partly or entirely replaced with ZnO plus Sb_2O_3, with equally good results. .13 equivalent of $ZnO+Sb_2O_3$ or SnO_2 is sufficient to produce a good white opacity by using two coats of white.

GENERAL CONCLUSION.

The conclusion on the ground coat and cover coats may be more specifically stated in formulae as follows:

Ground Coat Formula.

K_2O .15 to .75 Na_2O 0 to .6 CaO .14 to .64 CoO 0 to .06 MnO_2	}	Al_2O_3 .1 to .5	SiO_2 1.1 to 1.7 B_2O_3 .2 to .5

Cover Enamel Formula.

K_2O 0 to .60 Na_2O 0 to .65 CaO .2 to .60	}	Al_2O_3 0 to .5	SiO_2 1. to 1.8 B_2O_3 .2 to ?

In conclusion, the writer wishes to express his appreciation of the valuable assistance rendered by Mr. Lucian Shaw, C. E., in carrying out the experimental part of the work and in checking the calculations.

AN ATTEMPT TO CALCULATE THE AMOUNT OF HEAT UTILIZED FROM A DOWN-DRAFT KILN BY THE WASTE HEAT DRYING SYSTEM.

BY

A. V. BLEININGER Pittsburg, Pa.

In a test made some time ago the heat distribution of a down-draft kiln employed for burning hard building brick was calculated, based upon careful measurements of the kiln and exit temperatures, the composition of the waste gases, the fuel and the ashes, together with the weight of the coal and of the ware. The result was summarized as follows:

Heat lost by the fuel gases	27.33%
Theoretical Heat required to burn the bricks	19.55%
Heat lost by unburnt carbon in ash	3.51%
Heat taken up by kiln and lost by radiation	49.61%

At the close of the burn a 30-inch goose-neck was inserted into the door of the kiln which connected with an underground flue leading to the dryer. The air was thus drawn from the kiln by means of the large fan located at the dryer. A draft gauge was then connected with the goose-neck for determining the "head" caused by the pull of the fan. This was found to be quite uniform and equal to 14 divisions of the Richardson-Lovejoy petroleum gauge which corresponds to about ¼ inch of water by actual measurement. A thermo couple was likewise inserted into the goose-neck which was replaced later by thermometers. In this manner the temperature of the air leaving the kiln was carefully measured for 108 hours.

In attempting to calculate the amount of heat exhausted from the kiln by means of the fan we must know first the velocity of the air through the pipe. This it was only possible to approximate, since the draft gauge was not calibrated against an anemometer. The final value of the velocity accepted is lower than the actual velocity, since no attempt was made to use the Pitot tube correction factor, which is greater than unity. The theoretical velocity calculated from the head shown by the gauge, giving a lower value, was hence used, neglecting the decrease in the viscosity of the hot air and other factors due to cooling between the kiln and the fan. This, it is believed, did not introduce any significant error, since evidently the velocity was fairly uniform throughout the test. The velocity is thus calculated from the formula.

$$v = \sqrt{2\ g.\ h\ \frac{d_1}{d_2}}$$

v = velocity in meters per second.
g = gravity constant = 9.8 m.
h = head of water, expressed in meters = 0.00[illegible] m.
d_1 = density of air at 0° C.
d_2 = density of water at 0° C.

substituting we have

$$v = \sqrt{19.6\ .\ 0.006\ .\ 772} = 9.46 \text{ m.}$$

The velocity of the air was taken to be 9.5 m. per second.

The time was divided into nine periods of 12 hours each and the mean exit temperature calculated for every period. These were found to be as follows:

0 —	12	hours	885° C.
12 —	24	hours	715°
24 —	36	hours	640°
36 —	48	"	540°
48 —	60	"	435°
60 —	72	"	355°
72 —	84	"	265°
84 —	96	"	185°
96 —	108	"	135°

With a pipe diameter of 30 inches and using the velocity above calculated we have a discharge of 4.18 cu. m. per second or of 180,576 cu. m. during 12 hours. Owing

to the fact that the test was carried on during the dryest and hottest part of the summer, with an average temperature of about 20°, the humidity approximated at 50%. This figure is purely a guess, since the hygrometer was found to have been broken during transit. However, the introduction of the atmospheric moisture factor is not an important one, numerically. Assuming a vapor tension of 8.7 mm, the volume of steam introduced for the volume of air given above would be 2094 cu. m. The barometric pressure was taken to be 750 mm.

There remains now to calculate the weights of air and steam taken through the pipe for each period as well as the heat removed. This is illustrated for the first period as follows:

$$\text{Air....}180576\frac{273}{273+885}\cdot 1.275\cdot 865\cdot 0.237=11{,}127{,}000 \text{ kg. Cals.}$$

$$\text{Steam..}\ 2094\frac{273}{273+885}\cdot 0.797\cdot 865\cdot 0.48=\ 163{,}360 \text{ kg. Cals.}$$

Total heat removed by air and steam.....11,290,360 kg. Cals.

In this calculation 0.237 and 0.48 are the specific heats of air and steam respectively. Tabulating the results we obtain:

Period	Total number of kg. Calories
1	11,290,360
2	10,632,820
3	10,264,510
4	9,667,880
5	8,858,130
6	8,063,050
7	6,883,290
8	5,444,750
9	4,260,190
Total	75,364,980 kg. Cals.

The coal used during the burn had a calorific value of 6200. Hence the weight of coal equivalent to the amount of heat drawn from the kiln would be

$$\frac{75\ 364\ 980}{6200}=12155 \text{ kg. or}$$

26,741 pounds. During the entire burn 95,045 pounds of

coal were used. The heat exhausted from the kiln during cooling then equals 28.1% of the total heat introduced, so that the heat distribution could be rearranged as follows:

Heat lost by flue gases	27.33%
Theoretical heat required to burn the ware	19.55%
Heat lost by unburnt carbon in ash	3.51%
Heat stored by kiln and ware and recovered for drying purposes	28.10%
Heat lost by radiation and left in kiln and ware unused	21.51%
	100.00%

The recovered heat thus amounts to the equivalent of practically 400 pounds of coal per thousand bricks, or speaking more correctly, about 130 pounds of coal per ton of burnt clay, which is more than the heat theoretically required to burn the bricks. It is evident that not all of this heat is used in drying bricks, some of it is lost on the way to the dryer and in the latter itself. That a considerable amount of the heat is derived from the hot kiln walls is apparent from the comparison of the figures in the final distribution. Owing to the fact that this test was carried on in summer, the results show the most favorable conditions under which this particular kiln operates. In winter the heat actually available for drying would be considerably less, owing to the increased loss by radiation during cooling.

DISCUSSION.

Mr. Frink: I cannot agree with the writer that the factor of atmospheric moisture is an unimportant one, and hence I think the use of the hygrometer essential.

Mr. Bleininger: We did assume a humidity of fifty per cent and found by calculation it did not amount to more than one or two per cent difference.

MATT GLAZES.

BY

FREDERICK H. RHEAD, Oyster Bay, N. Y.

The glazes in question are the result of an attempt to produce a matt glaze with a broken surface, the glaze to mature at cone 1. The first series of glazes was based on the following raw glaze, with alterations as suggested by Prof. Purdy:

White lead	342
Cornwall Stone	90
Flint	90
Whiting	45
China Clay	22½
Tennessee Ball Clay No. 3	22½

The suggestions made by Prof. Purdy were to leave out the flint, decrease lead, and double the cornwall stone and whiting, add zinc, and substitute part of the whiting with plaster of paris. In the following series are glazes based upon this scheme but using felspar in place of cornwall stone.

SERIES I.

Glaze Number	White Lead	Feldspar	Whiting	Calcined China Clay	Tenn. Ball Clay No. 3	Zinc Oxide	Copper Oxide	Red Oxide of Iron	Plaster of Paris	Barium Carbonate	Flint
1	250	180	90	22.5	22.5	16	6	1	.....	.....	.....
2	200	180	90	22.5	22.5	16	6	1	.....	.....	.....
3	150	180	90	22.5	22.5	16	6	1	.....	.....	.....
4	100	180	90	22.5	22.5	16	6	1	.....	.....	.....
5	50	180	90	22.5	22.5	16	6	1	.....	.....	.....
6	250	200	90	22.5	22.5	16	6	1	.....	.....	.....
7	200	200	90	22.5	22.5	16	6	1	.....	.....	.....
8	150	200	90	22.5	22.5	16	6	1	.....	.....	.....
9	100	200	90	22.5	22.5	16	6	1	.....	.....	.....

SERIES I — CONTINUED.

Glaze Number	White Lead	Feldspar	Whiting	Calcined China Clay	Tenn. Ball Clay No. 3	Zinc Oxide	Copper Oxide	Red Oxide of Iron	Plaster of Paris	Barium Carbonate	Flint
10	50	200	90	22.5	22.5	16	6	1	.....	.....	.....
11	250	180	120	22.5	22.5	16	6	1	.....	.....	.....
12	200	180	120	22.5	22.5	16	6	1	.....	.....	.....
13	150	180	120	22.5	22.5	16	6	1	.....	.....	.....
14	100	180	120	22.5	22.5	16	6	1	.....	.....	.....
15	50	180	120	22.5	22.5	16	6	1	.....	.....	.....
16	250	180	90	40.	20.	16	6	1	.....	.....	.....
17	200	180	90	40.	20.	16	6	1	.....	.....	.....
18	150	180	90	40.	20.	16	6	1	.....	.....	.....
19	100	180	90	40.	20.	16	6	1	.....	.....	.....
20	50	180	90	40.	20.	16	6	1	.....	.....	.....
21	250	180	90	22.5	22.5	.....	6	1	.....	.....	.....
22	200	180	90	22.5	22.5	.....	6	1	.....	.....	.....
23	150	180	90	22.5	22.5	.....	6	1	.....	.....	.....
24	100	180	90	22.5	22.5	.....	6	1	.....	.....	.....
25	50	180	90	22.5	22.5	.....	6	1	.....	.....	.....
26	250	180	90	22.5	22.5	16	6	1	20	.....	.....
27	200	180	90	22.5	22.5	16	6	1	20	.....	.....
28	150	180	90	22.5	22.5	16	6	1	20	.....	.....
29	100	180	90	22.5	22.5	16	6	1	20	.....	.....
30	50	180	90	22.5	22.5	16	6	1	20	.....	.....
31	250	180	90	22.5	22.5	16	6	1	.....	25	.....
32	200	180	90	22.5	22.5	16	6	1	.....	25	.....
33	150	180	90	22.5	22.5	16	6	1	.....	25	.....
34	100	180	90	22.5	22.5	16	6	1	.....	25	.....
35	50	180	90	22.5	22.5	16	6	1	.....	25	.....
36	250	200	90	22.5	22.5	16	6	1	.....	25	.....
37	200	200	90	22.5	22.5	16	6	1	.....	25	.....
38	150	200	90	22.5	22.5	16	6	1	.....	25	.....
39	100	200	90	22.5	22.5	16	6	1	.....	25	.....
40	50	200	90	22.5	22.5	16	6	1	.....	25	.....
41	250	180	120	22.5	22.5	16	6	1	.....	25	.....
42	200	180	120	22.5	22.5	16	6	1	.....	25	.....
43	150	180	120	22.5	22.5	16	6	1	.....	25	.....
44	100	180	120	22.5	22.5	16	6	1	.....	25	.....
45	50	180	120	22.5	22.5	16	6	1	.....	25	.....
46	250	180	90	40.	20.	16	6	1	.....	25	.....
47	200	180	90	40.	20.	16	6	1	.....	25	.....
48	150	180	90	40.	20.	16	6	1	.....	25	.....
49	100	180	90	40.	20.	16	6	1	.....	25	.....
50	50	180	90	40.	20.	16	6	1	.....	25	.....
51	250	180	90	40.	20.	.....	6	1	.....	25	.....
52	200	180	90	40.	20.	.....	6	1	.....	25	.....
53	150	180	90	40.	20.	.....	6	1	.....	25	.....
54	100	180	90	40.	20.	.....	6	1	.....	25	.....
55	50	180	90	40.	20.	.....	6	1	.....	25	.....
56	250	180	90	22.5	22.5	16	6	1	10	.....	.....

SERIES I — CONTINUED.

Glaze Number	White Lead	Feldspar	Whiting	Calcined China Clay	Tenn. Ball Clay No. 8	Zinc Oxide	Copper Oxide	Red Oxide of Iron	Plaster of Paris	Barium Carbonate	Flint
57	200	180	90	22.5	22.5	16	6	1	10	25	.....
58	150	180	90	22.5	22.5	16	6	1	10	25	.....
59	100	180	90	22.5	22.5	16	6	1	10	25	.....
60	50	180	90	22.5	22.5	16	6	1	10	25	.....
61	250	180	90	22.5	22.5	16	6	1	.....	.....	40
62	200	180	90	22.5	22.5	16	6	1	.....	.....	40
63	150	180	90	22.5	22.5	16	6	1	.....	.....	40
64	100	180	90	22.5	22.5	16	6	1	.....	.....	40
65	50	180	90	22.5	22.5	16	6	1	.....	.....	40

The glazes were ground for five hours in a small pan color mill. No gummy medium was used in aplying the glazes to the trials, which were slabs of clay about 1.5 inch square.

Two bodies were used, an ordinary white body such as is used for colored glazes and a cane marl body. The white body was fired to cone 1 and the cane body to cone 06.

The slabs were dipped face downward into the glaze, the glaze being of such a consistency as to adhere to the surface of the tile, making a coating which is not less than a tenth and not more than an eighth of an inch in thickness.

Two trials of each glaze were fired in the kilns at the Roseville Pottery, one trial in the hardest and one in the easiest place.

The samples shown were selected after all the trials had come from the kilns. They are fair specimens of what the majority of those not shown were like.

It should be noted that the glaze surfaces will vary according to the condition of manufacture, however slight the variation in conditions may be. For instance, No. 33 was found to be very regular in all the experiments made by the writer, but it became a perfectly smooth matt glaze

NOTE BY EDITOR. — Mr. Rhead had several trials of his glazes on exhibition at the Convention. Those shown called forth many very complimentary remarks.

when made by another person and fired in kilns other than those used by the writer. A series of trials based on No. 3, however, resulted in glazes bearing the same markings, when the glaze was not subjected to too quick a fire.

The average time for firing for each kiln in which these trials were burned was thirty-nine and one-half hours.

Series II was based on the following glaze by Prof. Binns, published in an article appearing in Keramic Studio:

White lead	50
Feldspar	32
Barium Carbonate	12
China Clay	5
Flint	1

This glaze gave fairly satisfactory results in our regular kilns but the writer was desirous of determining whether a change in some direction would not result in a more perfect matt glaze. As no improvement was obtained the original formula was adopted as a basis of Series II. What I have designated here as Series II, instead of being a study in change in composition of glaze, is one in color effects produced by underglaze stains. Glazes of this Series II were made under the same conditions and fired in the same kilns as those for Series I.

The base glaze into which the coloring oxides and the underglaze stains were mixed to produce the variations shown in Series II was as follows:

White lead	100
Feldspar	64
Barium Carbonate	24
Cal. China Clay	10
Flint	2

SERIES II.

Number of Glaze	B2	B2A	B2B	B2C	B2D	B2E	B2F	B2G	B2H	B2I	B2J	B2K	B2L	B2M
Cobalt Oxide	6													
Marching's Crimson		10												
Purple			10											
Blue 156				10										
Faun 331					10									
Green 30						10								
Chrome Green							10							
Peacock 393								10						
Maroon									10					
Cardinal Red										10				
Pink 582											10			
Mulberry												10		
Dk. Yellow													10	
Lt. Yellow														10

The third series of trials is based on a glaze selected from the trials mentioned in Series II. The batch formula for the base glaze is as follows:

White lead	10 lbs.
Feldspar	3.5 lbs.
Barium Carbonate	1.5 lbs.
Cal. China Clay	0.5 lbs.
Flint	3 oz.

The variations shown in Series III are only those in colors, as here shown:

SERIES III.

No.	$MnCo_3$	CuO.	Fe_2O_3	CoO
OFF. 5	1.5 oz.	.....	.....	.....
OFF. 6	.....	2 oz.	0.5 oz.	4 Gr.
OFF. 7	.....	3 oz.	0.5 oz.	4 Gr.
OFF. 8	.....	4 oz.	1 oz	6 Gr.
OFF. 9	2 oz.	.....	.....	3 Gr.
OFF. 10	3 oz.	.....	.....	8 Gr.
OFF. 11	.....	.....	.....	1 oz.
OFF 12	11 Gr.	.....	.....	5 Gr.
OFF. 13	2 Gr.	.....	8 Gr.	2 Gr.

The fourth series of trials are double dips. The trials were dipped in the first glaze exactly as described previously for single dip, but with not quite so heavy a glaze. Before the first dip was quite dry it was dipped into the second glaze. The top glaze completely covered the under glaze and in no case did they mix. Rather a soft biscuit was used so that the glazes would dry almost immediately, allowing only sufficient time for the second dip. In every case the lower glaze was the heaviest, being about two-thirds of the total glaze thickness. In every case several trials were dipped in order to ascertain whether the biscuit was sufficiently soft and the glazes as used were of the right consistency.

While the least change in the method of double dipping will change the color effect this series of trials was more uniform than any of the single dip trials notwithstanding the variation in firing. It will be observed that there is a big difference in the double dips and the same dip reversed. This is to be seen in 9 and 10X, 11 and 12X, and 15 and 16X.

All these glazes are more or less sensitive, the tint varying considerable with change in condition of firing. But this does not mean that they are unreliable. It is unreasonable to expect that any glaze can be instantly adapted to any condition of manufacture, especially without an intelligent understanding of the condition. Quite often a glaze is altered when the formula is not to blame. The under and over grinding of the glaze, hard or soft biscuit, unskillful dipping, methods of firing and general factory methods are conditions which effect the glaze materially.

SERIES IV.

Number of Trial	Glazes Used.		
X	N.M.B	over	151A
XX	151A	"	N.M.B
XXX	121A	"	N.M.C.
4X	N.M.C.	"	121A
5X	N.M.B.	"	N.M.C
7X	121A	"	151A
8X	151A	"	121A
9X	B2A	"	B2B
10X	B2B	"	B2A
11X	B2H	"	B2G
12X	B2G	"	B2H
13X	B2E	"	B2G
15X	B2H	"	B2E
16X	B2E	"	B2H
17X	B2D	"	B2E
18X	B2E	"	B2D
25X	B2C	"	B2D
27X	B2H	"	B2D
28X	B2D	"	B2H
29X	B2D	"	B2F
30X	B2H	"	B2F
31X	B2I	"	B2F
32X	B2L	"	B2J
33X	2BK	"	B2L
34X	B2M	"	B2I

In Series V are a few glazes used in the double dips of Series IV, the formulae of which I have not as yet given. They are as follows:

SERIES V.

Glaze Number	121	121A	152	151A	151B	151C	NM	NMB	NMC
Fritt 121	16	16					420	420	420
White lead			150	150	150	150	5	5	5
Flint	2	2							
Whiting			30	30	30	30	5	5	5
Feldspar			57	57	57	57			
Cal. China Clay			40	40	40	40	7	7	7
Tenn. Ball No. 3			25	25	25	25			
Zinc Oxide	2	2	16	16	16	16	5	5	5
Barium Carbonate							5	5	5
Copper Oxide	0.25		6				6	6	
Marching's Blue No. 156		2							
Marching's Crimson				15				25	
Marching's Purple					10				25
Marching's Blue 156						15			

Fritt 121, mentioned in the above series, has as a batch formula the following:

Barium Carbonate	50
Feldspar	50
Fluorspar	30
Flint	20
Cal. China Clay	20
Borax	30

It is thought necessary to add that in using these glazes on pottery shapes, the glaze surface will vary ac-

cording to the shape used. The most marked difference is in Series III where the glaze, or broken solid portion of the glaze, hangs suspended from the top of the shape, leaving the lower portion of the glaze perfectly plain. There was no such separation in any of the other glazes.

Where more than one glaze is used, interesting effects have resulted from spraying the second glaze over the first, instead of dipping. Spraying of the second glaze, or splashing it, as is done with tin enamels to bead up colored glazes, produces unique effects. A red matt over a lilac matt is very interesting when treated this way. Another method is to dip in the usual way, and then dip the top of the piece in another glaze. This glaze, at the top, will run down and spread all over the surface, no two glazes behaving alike. For instance a red glaze for the body with a green top and the same green for body and the same red for top will behave in a totally different manner. The variation and behavior of these two glazes under these conditions were constant in character on repeated trials. See Vol. X.

DISCUSSION.

Mr. Purdy: Because Mr. Rhead has produced good matts of widely varying types, I calculated his batch formulae into molecular formulae.

Series I is divided into 13 sub-series as shown. Glaze No. 1 is reduced to unity RO. Where the other glazes in Series I differ from glaze No. 1, the fractional number of the varying molecule is given throughout the sub-group, without reference to sum of RO molecules. Where the fractional number of oxide molecule remains the same as in glaze No. 1, repetition sign is used. Glazes of the other series have RO = unity.

SERIES I.

Glaze No.	PbO	K_2O	CaO	ZnO	BaO	Al_2O_3	SiO_2	CuO	Fe_2O_3
1	.405	.135	.376	.082	.....	.208	.958	.032	.0026
2	.324	.135	.376	.082	.....	.208	.958	.032	.0026
3	.243	.135	.376	.082	.....	.208	.958	.032	.0026
4	.162	.135	.376	.082	.....	.208	.958	.032	.0026
5	.081	.135	.376	.082	.....	.208	.958	.032	.0026
6	.405	.150	.376	.082	.....	.223	1.046	.032	.0026
7	.324	.150	.376	.082	.....	.223	1.046	.032	.0026
8	.243	.150	.376	.082	.....	.223	1.046	.032	.0026
9	.162	.150	.376	.082	.....	.223	1.046	.032	.0026
10	.081	.150	.376	.082	.....	.223	1.046	.032	.0026
11	.405	.135	.502	.082	.....	.223	1.046	.032	.0026
12	.324	.135	.502	.082	.....	.223	1.046	.032	.0026
13	.243	.135	.502	.082	.....	.223	1.046	.032	.0026
14	.162	.135	.502	.082	.....	.223	1.046	.032	.0026
15	.081	.135	.502	.082	.....	.223	1.046	.032	.0026
16	.405	.135	.376	.082	.....	.232	1.003	.032	.0026
17	.324	.135	.376	.082	.....	.232	1.003	.032	.0026
18	.243	.135	.376	.082	.....	.232	1.003	.032	.0026
19	.162	.135	.376	.082	.....	.232	1.003	.032	.0026
20	.081	.135	.376	.082	.....	.232	1.003	.032	.0026
21	.405	.135	.376	.....	.....	.208	.958	.032	.0026
22	.324	.135	.376	.....	.....	.208	.958	.032	.0026
23	.243	.135	.376	.....	.....	.208	.958	.032	.0026
24	.162	.135	.376	.....	.....	.208	.958	.032	.0026
25	.081	.135	.376	.....	.....	.208	.958	.032	.0026
26	.405	.135	.425	.082	.....	.208	.958	.032	.0026
27	.324	.135	.425	.082	.....	.208	.958	.032	.0026
28	.243	.135	.425	.082	.....	.208	.958	.032	.0026
29	.162	.135	.425	.082	.....	.208	.958	.032	.0026
30	.081	.135	.425	.082	.....	.208	.958	.032	.0026
31	.405	.135	.376	.082	.0531	.208	.958	.032	.0026
32	.324	.135	.376	.082	.0531	.208	.958	.032	.0026
33	.243	.135	.376	.082	.0531	.208	.958	.032	.0026
34	.162	.135	.376	.082	.0531	.208	.958	.032	.0026
35	.081	.135	.376	.082	.0531	.208	.958	.032	.0026
36	.405	.150	.376	.082	.....	.223	1.046	.032	.0026
37	.324	.150	.376	.082	.....	.223	1.046	.032	.0026
38	.243	.150	.376	.082	.....	.223	1.046	.032	.0026
39	.162	.150	.376	.082	.....	.223	1.046	.032	.0026
40	.081	.150	.376	.082	.....	.223	1.046	.032	.0026
41	.405	.135	.502	.082	.0531	.208	.958	.032	.0026
42	.324	.135	.502	.082	.0531	.208	.958	.032	.0026
43	.243	.135	.502	.082	.0531	.208	.958	.032	.0026
44	.162	.135	.502	.082	.0531	.208	.958	.032	.0026
45	.081	.135	.502	.082	.0531	.208	.958	.032	.0026
46	.405	.135	.376	.082	.0531	.232	1.003	.032	.0026
47	.324	.135	.376	.082	.0531	.232	1.003	.032	.0026
48	.243	.135	.376	.082	.0531	.232	1.003	.032	.0026
49	.162	.135	.376	.082	.0531	.232	1.003	.032	.0026
50	.081	.135	.376	.082	.0531	.232	1.003	.032	.0026

GlazeNo.	PbO	K_2O	CaO	ZnO	BaO	Al_2O_3	SiO_2	CuO	Fe_2O_3
51	.405	.135	.376	.....	.0531	.232	1.003	.032	.0026
52	.324	.135	.376	.....	.0531	.232	1.003	.032	.0026
53	.243	.135	.376	.....	.0531	.232	1.003	.032	.0026
54	.162	.135	.376	.....	.0531	.232	1.003	.032	.0026
55	.081	.135	.376	.....	.0531	.232	1.003	.032	.0026
56	.405	.135	.401	.082	.0531	.208	.958	.032	.0026
57	.324	.135	.401	.082	.0531	.208	.958	.032	.0026
58	.243	.135	.401	.082	.0531	.208	.958	.032	.0026
59	.162	.135	.401	.082	.0531	.208	.958	.032	.0026
60	.081	.135	.401	.082	.0531	.208	.958	.032	.0026
61	.405	.135	.376	.082	.....	.208	.123	.032	.0026
62	.324	.135	.376	.082	.....	.208	.123	.032	.0026
63	.243	.135	.376	.082	.....	.208	.123	.032	.0026
64	.162	.135	.376	.082	.....	.208	.123	.032	.0026
65	.081	.135	.376	.082	.....	.208	.123	.032	.0026

BINN'S MATT GLAZE (CONE 1).

USED IN SERIES II.

$$\left.\begin{matrix}0.621\ PbO\\0.184\ K_2O\\0.195\ BaO\end{matrix}\right\}\ 0.246\ Al_2O_3 \qquad 128\ SiO_2$$

BASE GLAZE FOR SERIES III.

$$\left.\begin{matrix}.737\ PbO\\.120\ K_2O\\.144\ BaO\end{matrix}\right\}\ .157\ Al_2O_3 \qquad .85\ Sio_2$$

Fritt 121 used in Series V.

$$\left.\begin{matrix}0.315\ BaO\\0.111\ K_2O\\0.476\ CaO\\0.097\ Na_2O\end{matrix}\right\}\ .207\ Al_2O_3 \qquad \left\{\begin{matrix}1.271\ SiO_2\\0.194\ B_2O_3\end{matrix}\right.$$

comb. wt.[1]=202.25

SERIES V.

Molecular formula of base glaze in 121 and 121A B:

$$\left.\begin{matrix}0.238\ ZnO\\0.240\ BaO\\0.086\ K_2O\\0.074\ Na_2O\\0.362\ CaO\end{matrix}\right\}\ 0.16\ Al_2O_3 \qquad \left\{\begin{matrix}1.29\ SiO_2\\0.15\ B_2O_3\end{matrix}\right.$$

[1]No allowance for loss of SiO_2 as SiF_2 or for retention of the fluorine. Reports of investigations indicate that in glasses in which cryolite or fluorspar is an ingredient, the fluorine is retained on quick melting and largely expelled as SiF_2 on long firings. No reliance can be had in assumptions as to SiO_2 or Fl content in a given case even when conditions attending the melting are known.

Molecular formula of base glaze in 152, 151A, 151B, 151C:

$$\left.\begin{matrix}0.492\ PbO\\0.254\ CaO\\0.087\ K_2O\\0.167\ ZnO\end{matrix}\right\}\ 0.30\ Al_2O_3\qquad 0.948\ SiO_2$$

Molecular formula of base glaze in N. M., N. M. B., N. M. C.:

$$\left.\begin{matrix}0.304\ BaO\\0.103\ K_2O\\0.465\ CaO\\0.090\ Na_2O\\0.009\ PbO\\0.028\ ZnO\end{matrix}\right\}\ 0.205\ Al_2O_3\qquad \left\{\begin{matrix}1.21\ SiO_2\\.18\ B_2O_3\end{matrix}\right.$$

The following notes concerning the trials exhibited by Mr. Rhead may add to the value of his contribution:

SERIES I.

Glazes 26-28 incl. are badly cracked, not healed and have incipient gloss.

Glazes 31—34 incl., 36—38 incl., 41—42 incl. are flaked nicely, healed perfectly and are true matts.

Glaze 43 cracked badly and not healed, true matt.

Glazes 46 to 47, perfectly smooth matts.

SERIES II.

The Binns matt flaked to a slight extent in some cases and in others not very appreciably. They are all good matts, however, though some are overloaded with the color stain.

SERIES III.

These are all beautiful matts with striking crackeled or flaked effects. The colors in this series are uniformly good.

SERIES IV.

Mr. Rhead's description of this series is ample. Some very good effects are obtained by the two-color dip.

SERIES V.

Glazes 121 and 121A have incipient glass; are not good matts.

Glazes 152, 151A and 151B, are beautiful, having very handsome water line or flaking effects.

Glazes N. M., N. M. B., and N. M. C. are dry in appearance and are wrinkled up in wave form. No flakes apparent.

The only factors known to me which seem to control this flaking, or separation in matt glazes were developed in experiments based on a cone 1 matt having a molecular formula as follows:

$$\left.\begin{matrix} 0.08\ KNaO \\ 0.52\ PbO \\ 0.39\ CaO \end{matrix}\right\} \quad 0.34\ Al_2O_3 \quad 1.2\ SiO_2$$

In these experiments it was indicated that:

(1) Flakes decreased in size with *in*crease of SiO_2.

(2) Flakes decreased in size with *de*crease of AlO_3.

(3) Flakes decreased in size with *de*crease of CaO.

Mr. Rhead's experiments check these observations very nicely. His experiments indicate an additional factor in this flaking phenomenon, that BaO is more potent than CaO in producing flakes.

Inasmuch as no good matts without ZnO were obtained by Mr. Rhead, no conclusion concerning the effect of ZnO on flaking can be drawn.

It is important to note that the oxygen ratio (1.1—1.4) of the true matt glazes made by Mr. Rhead (as in the case of others of which I know) is very much lower than that given by Prof. Orton as being safe with his RO[1] at cone 1 or 2. In fact their oxygen ratio is lower or as low as those which Prof. Orton obtained at cone 10.

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[1]See page 566, Vol. X. A. C. S. Trans.

DISCUSSION.

Mr. Jackson: To what is the flaking due in these trials? My experience with the formulae on the board, or on similar lines, would lead me to believe that Professor Binns' formula would have the least flaking of all.

Mr. Purdy: That is true.

Mr. Jackson: And in the paper it is stated the other way, that more was noticed in his formula than in any of the rest. Is it true, then, that in Professor Binns' formula less flaking occurs?

Mr. Purdy: Flaking is not so prominent in Prof. Binns' formula as in the others.

Mr. Binns: Mr. Chairman, there are a good many points in connection with this investigation which might be dilated upon. First of all, is the question of flaking. I have always attributed this to a cracking of the drying glaze and a healing over at the joints. There may be cases where this is not true, but I think that in many, if not in the majority of cases that is what takes place, and the sample which I saw just now tends to prove that contention. It is exactly what we are familiar with when glazes are put on thick, and are slow to fuse. The reason I asked the question as to whether it could be produced equally well on a vertical surface is that frequently results may be produced on a flat surface that would be impracticable on a vertical surface. This is not due in any instance to the chemical formula. It may be produced by an excess of clay, by an unduly thick glaze, by too finely grinding the glaze, and by a number of conditions none of which are taken cognizance of in the chemical formula. I think it is purely a mechanical condition. I think I could in all glazes produce all grades of flaking simply by mechanical mixing of the formulae.

This paper tends to prove that Professor Orton's contention was right, that the higher the temperature the lower the oxygen ratio; at the high temperatures the glaze

will feed more upon the body surface. Therefore, a lower oxygen ratio becomes necessary.

There is one point I may be pardoned for mentioning, which may call up another discussion that I am not anxious to precipitate, and that is the position of boric acid. In regard to the introduction of B_2O_3, if this be placed in the acid position, the oxygen ratio appears unusually high for a matt glaze; but if placed in the R_2O_3 column the glaze falls into the normal ratio of the sesquisilicate.

Mr. Gates: Mr. President, my experience leads me to agree with Professor Binns that flaking marking is a mechanical matter. It depends on the thickness of the glaze, and the flaking comes from incipient cracking of the glaze before firing. I do not think there is any doubt about that. It is partially healed over in the burning.

Mr. Walrath: If it is purely a mechanical process, why does not this flaking show in all the glaze formulae? In my experience I have found that in many instances this cracking shows after the glaze is applied, but disappears after firing; but in many glazes we can hold the flaking so it will show.

Mr. Jackson: Mr. Walker gave me quite an experience after the Cleveland meeting, in regard to matt glazes. The first thing I was up against was this flaking or cracking. He did not state in his paper whether he used raw or calcined clay; so I tried it with the alumina content as raw clay on vertical and horizontal surfaces. On both vertical and horizontal surfaces I had a beautiful crackle. I then used the calcined clay in the same formula and after that had no difficulty with the cracking, showing that the only difference between that which was cracked and that uncracked was the use of calcined and raw clay, the one fusing and healing over, after the cracking.

The Chair: In your case it was a case of shrinking of the clay substance in the glaze which started the crack.

Mr. Jackson: Yes, the raw clay substance in shrinking started the cracking.

The Chair: And the calcining overcame that shrinkage and overcame the cracking.

Mr. Gates: That answers the question and is exactly the experience I had — controlling the shrinkage of the glaze and then the thickness of the glaze; and also if the glaze was very fusible I might have the cracking appear in the glaze when it was just dipped, but the fusibility of the glaze might heal it later on. But calcining the clay would often do away with the trouble.

Mr. Walrath: That was not my experience. I got some of the best crackle with calcined clay.

The Chair: I think that depends entirely upon the ratio between glaze and body. Were you using raw or biscuit body?

Mr. Walrath: Either raw or biscuit.

Mr. Ashley: Mr. President, if I remember rightly, some years ago in a discussion Mr. Stover spoke of a glaze which gave him trouble by scaling off or something of that sort; and he stated that he got rid of the trouble by not using over the water in the slip house. Perhaps Mr. Stover can tell us more about that and throw some light on this problem.

Mr. Storer: I do not think it has any relation to this particular series of trials. We had flaking off and found we could remedy it by not using over the slip water.

Mr. Weelans: Mr. President, I would like to add my testimony to the effect that I believe, as Mr. Binns said, it can be attributed to many causes. Of course, I am not acquainted with the practice in low fire glazes, but in our experience, we have noted various causes for this trouble of glaze separation or flaking, some of which are as follows:

First: In vitreous ware when glazed with a brush and a number of applications are required to obtain the necessary thickness, each coat of glaze should be sufficiently dried out before another one is applied. If not,

this fault occurs, and is due to contraction of the upper coats of glaze in drying out (mainly by evaporation) before the undercoats have had opportunity to dry, owing to lack of absorption of vitreous body. Very fine cracks are thus formed on the surface, which when glaze is thoroughly dried out, extend through entire thickness of glaze. If each coat be thoroughly dried out, considerable thickness of glaze can with safety be used.

Second: When glaze is dipped too heavy. The cause being the same as in No. 1.

Third: When the glaze is what is commonly termed "too hard" for the temperature used — too high content of alumina, for example.

Fourth: There are still causes not thoroughly understood other than chemical, and which occur in the use of the same batch of glaze and which in some factories I am informed occasioned much trouble and expense. When we experienced this difficulty, we attributed it to the first cause recited above, and remedied it by increasing the heat in the work shop to warm up the ware to be glazed and increasing the number of pieces proportioned to each man, thus lengthening the time between each application.

Mr. Binns: I would like to add a word before the discussion is closed, because I think there is a good deal of truth in Mr. Walrath's contention. I stated, a little unadvisedly, perhaps, that I could produce the effect in any glaze by mechanical treatment. I am not sure that I could now; but I think in a great many glazes it can be produced. I think where we have a highly fusible matt healing over, it would be hard to notice the cracks. In other cases, as in a glaze with a high content of barium, the healing shows very markedly after burning. I think this behavior of barium has been mentioned before. It is a fact stated by competent authorities that barium carbonate parts with its carbon dioxide very slowly, taking a very high temperature for it to enter into solution.

Mr. Hastings: One depends on the higher amount of lime for its matt and Professor Binns is depending on high alumina; and I find where the glaze has a large amount of lime it will show this kind of surface. If the glaze is sprayed on instead of being dipped this disappears, showing that the mechanical application of the glaze has much to do with this effect.

Mr. Elcod: I submit my experience in regard to flaking (surface cracking) and preventing same — without changing the composition of the glaze. By making a matt glaze base, for colored matt glazes for tiles, I have oversaturated a raw glaze with oxide of zinc; by doing that I suffered from flaking (broken-up-surface). I have tried to use different oxide of zincs, but flaking was there always, more or less. And I wanted to use oxide of zinc in my glaze, for the reason that certain colors can be obtained only with ZnO, as for instance, certain blues. Therefore, I have tried to calcine a portion of the raw glaze, with the whole amount of ZnO in it, at a low red heat, at about cone 018. At this temperature the calcine could be easily powdered up between the fingers and was easily ground fine with the rest of the glaze. By doing that, I have overcome flaking, without changing the composition of the glaze.

NOTES ON BOLTING CLOTH SIZES.

BY

H. E. ASHLEY, Pittsburg, Pa.

In our *Transactions,* mention is frequently made that a glaze or body has been sieved thru a lawn of a certain number. It is often not stated how many meshes to inch this corresponds to, and occasionally an incorrect statement of the number of meshes per inch is made.

In order that our *Transactions* may have an authoritative record of the meaning of such sizes, I have collected the following table from the trade circulars of three leading manufacturers.

SIZES OF SWISS SILK BOLTING CLOTHS AS GIVEN BY THE MANUFACTURERS. MESHES TO THE INCH.

No.	Dufour & Co.'s "Old Anchor" Brand.	Bodmer's "Old Reliable."	Reiff-Franck's Swiss Silk.
0000	18	18	18
000	22	22	22
00	29	28	28
0	38	38	38
1	48	48	48
2	54	52	52
3	58	56	56
4	62	60	60
5	66	66	64
6	74	72	72
7	82	80	80
8	86	84	84
9	96	96	94
10	108	108	106
11	116	116	114
12	124	124	124
13	128	130	130
14	140	139	139

No.	Dufour & Co.'s "Old Anchor" Brand.	Bodmer's "Old Reliable."	Reiff-Franck's Swiss Silk.
15	150	147	148
16	156	157	156
17	164	164	163
18	168	172	173
19	172	.....	183
20	176	.....	192
21	182	.....	.....

DISCUSSION.

Mr. Ashley: I may say, too, that the number of the cloth does not give the whole story as to size of particles passed thru the lawn. That is, it may be Standard, Extra Heavy X, Double XX, or Treble Extra XXX, and in the latter case the particles passed are decidedly smaller than in the former case, heavier threads being employed.

A brass lawn of 130 meshes to the inch will pass the same size particles as a 12XX silk lawn of 124 meshes to the linear inch, etc.

Mr. Parmelee: I would like to add my confirmation of what Mr. Ashley has said as to samples of brass bolting cloth. I have counted the meshes and found that in the higher numbers, the numbers did not indicate anything at all of value.

Mr. Purdy: You can see that on the same sheet, if you buy a number of yards. It seems it is a mechanical fault in the making.

Mr. Parmelee: I think it is in the size of the wire also.

Mr. Binns: I am glad this subject has come up. I think the first time it appeared in our *Transactions* was in a paper of Mr. Krehbiel of the New York State School, in which he gave the sizes of the openings in the lawn. I think it would be best to have accuracy and to devise some method of naming and numbering lawns according to the size of the mesh.

Mr. Stover: I think when you speak of particles passing a certain size lawn, it does not tell the story unless you state the extremes. We often find in making experiments that very fine and very coarse would not give the result, but a certain percentage of each will give the result. We should state the average or extremes and quality of each.

Mr. Ashley: A thick slip going thru a lawn will not pass as coarse particles as a thinner slip. The thinner slip will go thru quicker than the thicker slip where it goes thru all day long.

Mr. Tone: The designations of the makers of bolting silks are, as Mr. Ashley states, a very unsafe indication of the actual mesh of the cloth. In standardizing bolting cloths for the grading of carborundum and other materials, I have found it necessary, not only to count all cloths in both directions, but also to accurately measure the sizes of the openings. The cloth rarely shows the same count as that stated by the maker, and furthermore, it never counts the same in two directions. Two cloths may count the same, but differ in the screened product which they pass, on account of the different sizes of the threads. The counting of cloth up to 100 or 120 meshes is a simple matter with the aid of the microscope. For the finer meshes we have had recourse to a method which I have never seen previously described.

A simple form of cheap projecting lantern is employed, the slide having an aperture ½ inch square, over which a piece of the cloth to be tested is placed. The image is thrown on a screen about six feet away and is magnified about thirty-six times. The mesh is then counted and the sizes of the openings are measured in both directions in millimeters. Several openings are measured, and the averages taken. It is possible also to measure the size of thread and to note the regularity and shape of the openings. Some results on the very finest meshes produced by several lead-

ing Swiss manufacturers may be of interest and are given below:

Maker.	No.	Count per inch.	Size of opening mm.
A	20	192 x 200	.065 x .070
B	20	162 x 180	.080 x .072
C	21	172 x 198	.050 x .072
C	22	172 x 230	.036 x .048
D	25	182 x 202	.065 x .075

I would strongly urge anyone who wishes to maintain any standards or do any accurate work with the finer numbers of silk in the testing laboratory or even in regular manufacturing operations to use this or some similar method of measuring the actual size of the openings in the cloth.

A COMPARISON OF POTASH AND SODA FELDSPAR PORCELAINS.

BY

A. S. WATTS, Victor, N. Y.

A statement has often been made in my hearing to the effect that soda spar, or Albite, cannot be successfully used in the manufacture of white ware or granite ware, owing to the fact that the ring of the ware is like that of wood, whereas, with potash spar, or Orthoclase, the ring of glass is obtained. A thorough investigation of this subject among pottery manufacturers convinces me that the statement is correct. However, I know of no one who has experimented with soda spar in porcelain manufacture and as I find no record in our *Transactions* of such experiments, I am offering you my experience along this line in the hope that others who have had experience with soda spar may come forward and add their data on the subject.

In my investigation I used spars having formulae approximately as follows:

CANADIAN POTASH SPAR "T."

.784 K_2O .176 Na_2O .022 CaO .017 MgO	1.01 Al_2O_3 .008 Fe_2O_3	5.79 SiO_2
.999		

CONNECTICUT POTASH SPAR "U."

.5665 K_2O .3751 Na_2O .0165 CaO .0424 MgO	.89 Al_2O_3 .022 Fe_2O_3	6.29 SiO_2
1.0005		

MARYLAND SODA SPAR "V."

.011 K_2O		
.637 Na_2O	1.066 Al_2O_3	5.38 SiO_2
.042 CaO	.019 Fe_2O_3	
.304 MgO		
.994		

I made bodies using these spars and gave to the body produced the letter of the spar it contained, viz.:

"T" body contains Canadian Potash Spar "T."
"U" " " Connecticut Potash Spar "U."
"V" " " Maryland Soda Spar "V."

The bodies produced had approximately the composition:

.16 KNaO		
.08 CaO	1.00 Al_2O_3	4.5 SiO_2

being made up as follows:

Feldspar	21.35
Whiting	2.00
Eng. China Clay	43.92
Eng. Ball Clay	8.
Flint	26.73
	102.00

The bodies were made up into bell-shaped cups in order that the ring of the ware might be observed to best advantage. These cups are 4 inches high, 4 inches in diameter at mouth, and .2 inch in thickness. They were fired at cone 10 in a normal atmosphere. No warping was apparent in any of the bodies. So far as appearance is concerned I can not note any difference in vitrification between the different bodies, although "T" body has the best color due to its lower iron content.

A test of the tone produced by striking the different cups indicates very plainly the difference due to the spars used. The soda spar body "V" has a short ring like the sound produced by striking a glass nearly filled with

water. Both the potash bodies "T" and "U" have lower rings, similar to a glass either empty of nearly so. It is difficult to determine which of the latter two is superior in this quality.

What the cause of this difference may be, is difficult to determine, but it seems to be a case of the soda spar body absorbing the shock while the potash spar bodies repel the shock, thus producing a clearer sound and one of longer duration. If this is the case it would naturally be assumed that the soda spar body would withstand a sudden strain better than the potash spar body. To test this property I proceeded to subject the three bodies to a series of sudden temperature changes, by heating and then plunging into ice water.

The test was begun at 300°C. and the water for chilling was maintained at as near 5°C. as possible. These tests

were made at intervals of 50°C. until 950° was reached, no evidence of weakness being noted in any of the bodies. When the heat was raised to 1000° however, all three bodies after chilling proved weak and could be broken between the fingers. On raising the temperature to 1050° this property was strikingly notable, all the bodies being now thoroughly friable, breaking into small irregular blocks on the least pressure. I note, however, that a small area midway between the two outside walls of the piece retains its smooth fracture indicating that the phenomenon is due to the sudden cooling and this is further proven by the fact that trials subjected to the same heat treatment, but cooled in air, are not injured in any way.

If this phenomenon is due to a vesicular structure it would be indicated by its power to resist the electric current. To prove this the various bodies were subjected to electrical test, about 20 tests being made on each body. The result was practically uniform in every case, the variation being in every case within the variation limits of commercial tests.

A study of the chemical compositions of the various feldspars brings to my attention the fact that the soda spars contain a far higher per cent of MgO than do any of the potash feldspars and also the fact that the soda spars contain a lower percentage of true alkali (K_2O and Na_2O) than do the potash spars.

Regarding the influence of MgO, I find that there is at present being made in the United States, a good porcelain containing potash spar and a greater amount of magnesium oxide than could be introduced by the use of any known soda spar. This porcelain has an excellent ring.

Regarding the influence of a lower percentage of true alkali, I find that good porcelains can be made with as low as 12 per cent of feldspar while these bodies contain 21 per cent. Hence the amount of true alkali in a 12% spar body would be as low as is found in the soda spar body and, moreover, the soda spar body possesses excel-

lent translucency, which indicates that the alkali is present in sufficient quantity for that purpose at least.

The difference cannot be due to any other ingredient than the feldspar since all other ingredients are identically the same in every body tested both in quality and quantity. If the solution to this problem is not found in some of the possible explanations offered here I conclude that the difference between the sound obtained is due to some inherent property possessed by either potash or soda spar and not possessed by the other. The microscope does not solve this problem, although a very interesting phenomenon is noted, i. e., that the soda spar porcelain contains groups of minute bubbles similar to those observed in overfired potash porcelains, or in porcelains extremely high in alkaline fluxes. That this should be the cause of this difference in sound obtained is hardly to be credited, since an over-fired potash porcelain invariably has a very clear bell-like sound, even superior to that obtained at the proper commercial firing.

Since a soda spar porcelain is to all appearances equal in all the above properties to the potash spar porcelain, it appears to me to offer a means of cheapening the cost of many bodies where this particular quality of sound does not represent any value. Care must be exercised, however, that the grinding is carried to the same degree as with the potash spar, otherwise the economy obtained from its lower fusing point and its lower cost will be largely lost.

DISCUSSION.

Mr. Richardson: Did you notice any difference in the toughness of the two bodies?

Mr. Watts: I did not test it particularly for toughness. My experiments, with a view to making an impact test, have not been an entire success. It seems that the mechanical devices we have at present cannot be well applied to the porcelains or pieces already made, so I have not made any successful impact tests.

Mr. Frink: Have you made a test by grinding it down and examining it by a microscope?

Mr. Watts: I have to 1/1000 of an inch, to where it was transparent.

Mr. Frink: Did you get any tables from it?

Mr. Watts: Yes, sir.

Mr. Frink: We have made experiments and find we have lower rings with soda glass, and when mixed we find the notes are very similar.

Mr. Stover: The difference in the ring may come from the difference in the elasticity of the material. Soda is 100 and potash 71 and will give a very high note. Magnesia has an elasticity factor of 600.

CRYSTALLINE STRUCTURE IN PORCELAINS.

BY

ARTHUR S. WATTS, Victor, N. Y.

Concerning the history of porcelain investigations, I find by the writings of Plenske that Ehrenberg in 1836 observed that the kaolin and flux lay near one another in a milky appearing mass, the flux forming the transparent portion and the opaque kaolin in the form of globules strung one after another, while crossing in all directions, woven one into another, appear tiny straight sticks. In 1847, Oschatz and Wachter offered data tending to prove that porcelain consists of a glassy matrix filled with innumerable fine crystals, which so reflect and refract the light as to cause the body to appear opaque. Behrens, in 1873, confirmed these investigations, but held that the refraction of light is largely due to the presence of quartz splinters, which he found exists in great quantities, especially in Berlin porcelains. In 1876, Truax came forward with the claim that porcelain is a mechanical mixture of uncombined quartz and kaolin particles, the intervening spaces being filled by the molten but not chemically combined feldspar.

Hussaks found crystalline structure in high fire porcelain and stated in 1889 that he was impressed with their similarity to Sillimanite. Mellor also found crystalline structure in Chinese and Berlin porcelains, in a fire brick and in a slag from Vesuvius. Vernadsky, in 1890, came forward with the observation that in different porcelains there exists apparently prismatic crystals, optically positive, disappearing in polarized light parallel to the prism faces and insoluble in cold HF. Through isolation by means of HF,

H_2SO_4 and neutralization through $(NH_4)_2\ CO_3$, decantation and washing, Vernadsky found in Sevres porcelain 35% crystallite, which had the composition 29.7 SiO_2 and 70.3% Al_2O_3. This corresponds to the formula 11 Al_2O_3 8 SiO_2. Vernadsky held, however, that some powdered alumina was also present and that the needle crystals were really Sillimanite, i. e., $Al_2O_3\ SiO_2$.

Vernadsky later obtained isolated crystals, which by analysis showed a composition of 37.31% SiO_2 and 63.65% Al_2O_3, which gives practically a formula of $Al_2O_3\ SiO_2$. He also obtained Sillimanite crystals from andalusite, cyanite, topaz, and other minerals at 1320° to 1380° heat, and excellent crystalline structure was obtained by heating a mixture of pulverized alumina and silicic acid, in the proportions 1 mol. Al_2O_3 to 2 SiO_2. Plenske also found in fluxed Zettlitz kaolin a formation of crystallite in the amorphous mass.

From the great resemblance of the crystal needle obtained in the molten minerals to the crystallite obtained in burned clay, alumina-silicic acid mixture and in the different porcelains, Vernadsky came to the conclusion that "All clayware is through sufficiently severe burning filled with Sillimanite crystals."

Glasenapp, from his study of the microstructure of clayware and kaolin and apparently without any knowledge of the observations of Vernadsky and others, makes this statement of his conclusions: "All clay is, in sufficiently high temperature under dissociation of the clay substance, crystalline." It exists as a glassy matrix and a crystalline portion, and since the fusibility of the aluminum silicate decreases with the silicic acid content, Glasenapp thinks that the crystalline portion is rich in alumina and the amorphous portion is rich in silica.

Just how the process of crystallization and re-construction occurs, we may only infer from the varied opinions offered. Plenske finds that where neither the pure

kaolin nor the pure feldspar contain crystallite, the formation of Sillimanite may occur in the presence of two materials heated together, and he can only explain this through the chemical influence of the molten feldspar on the amorphous Al_2O_3 $2SiO_2$. He finds also that an addition of 1—2% basic substance as alkali or lime promotes the decomposition of the Al_2O_3 2 SiO_2, and hence encourages the crystalline formation. The addition of a small amount of magnesia gives much more beautiful crystals. Plenske also notes the importance of the rate of cooling on the resultant product. The action of the burning process on the constituent ingredients is well explained by Behrens, who from microscopic investigation concluded that the clay substance, on account of its small grains and amorphous condition, is more dissolved by the molten feldspar than is the quartz.

By the firing of a porcelain containing quartz most of the quartz particles are externally dissolved and covered with a coating of silicate preventing any further attack, and resulting in the matrix never becoming sufficiently fluid for a diffusion of the different silicates.

Plenske finds, as a result of investigations carried on, that about the only certainty established is that the kaolin is dissolved by the molten feldspar. He further notes that the crystallization in many porcelains is distributed throughout the entire mass, while in others it is only noted in groups or isolated appearances. It appears, therefore, no positive statement can be based on observations of the porcelain structure.

Zoellner in his investigations went more into detail, so far as the action from different clays were concerned. He tested seven specimens of kaolin and clay and from the resultant masses determined the percentage of Sillimanite present. I give below a table showing this data:

		Zittlitzer Kaolin	Kemmlitzer Kaolin	Poschez Kaolin	Wiesauer Erde	Hallescher Ton	Wildstein Ton	Putschirner Ton
	% Sillimanite Residue	20.5	21.12	22.4	18.9	14.3	2.1	5.8
Complete Analysis	H_2O	13.00	11.82	13.42	9.67	14.74	11.20	12.10
	KNaO	.66	.49	.83	2.20	.....	3.02	1.70
	MgO	.38	.13	.22	.52	.11	.10	.20
	CaO	.80	.17	.20	.90	.12	.25	.....
	Fe_2O_3	.90	.29	.80	1.76	1.25	2.20	.....
	Al_2O_3	38.54	32.90	39.23	33.69	37.90	35.70	30.00
	SiO_2	45.66	54.20	45.66	51.33	45.90	47.70	56.00
Rational Analysis	% Feldspar	.....	.51	.....	2.24	.....	1.06	.....
	% Quartz	1.	14.80	1.00	12.56	.....	2.22	.....
	Clay Substance	99.	84.60	99.0	85.20	.....	90.70	.....

As a result of his investigation, he says: "One will not go wrong when one asserts that the amorphous product of the neutral mass, is converted into a portion rich in silicic acid and a crytalline portion, which is a rich aluminum silicate."

He quotes Hecht as explaining the different limits of soft and hard porcelains from the existence of an undissolved quartz, but expresses a doubt if the decomposition of the quartz alone is sufficient to bestow on the burned mixture the characteristics of porcelain. Also Geo. Vogt, Director of the National Manufacturers of Sevres, observes in this connection that one and the same mass burned at different temperatures displays different characteristics. Zoellner finds that the transparency and the fracture are greatly influenced by sillimanite structure. He finds that

the specimens without sillimanite structure exhibit a faint earthy yellow translucency and granular fracture, while those with sillimanite structure display highly uniform bluish-white translucency and a smooth fracture. In his investigations he accumulates data which leads him to the following conclusions:

Feldspar is able, in the heat of the porcelain kiln, to dissolve 3.5% alumina, 14% clay substance, and 60 to 70% quartz. This ratio does not alter where more than two components go into reaction.

Microscopic investigation indicates that at Seger cone 15 — 16, feldspar porcelain consists of a glassy matrix, filled with plentiful needle crystals, violently corroded quartz and many gas bubbles.

The minute structure of low fired porcelain, i e. to cone 12 — exhibits melted feldspar, corroded quartz, and an amorphous silicate, probably anhydrous clay substance, — all lying close together.

The analysis of the crystalline portions from two different porcelains, and a high-fired Seger porcelain, give a ratio of Al_2O_3 to SiO_2 as 1 : 1. The crystals are undoubtedly Sillimanite.

Concerning the formation of Sillimanite, Zoellner concludes by stating that in the *Seger kiln* it develops at Seger cone 13 (about 1400°). In the porcelain kiln, however, the development may occur at 1350°—1370° on account of the longer time of burning. He says, however, that they do not form below 1350°. In the porcelain kiln all of the Sillimanite is formed from the kaolin.

The origin of Sillimanite depends not on a devitrification phenomena, but from a molecular alteration of the clay substance. The splitting of the clay substance into an amorphous silicate, rich in silicic acid, and a crystalline silicate, rich in alumina, is hastened by the working of the flux.

Zoellner reaches the following industrially important conclusions:

He confirms the established impression that it is necessary to advance to higher temperatures to obtain a good product.

The optical or chemical investigation gives a method by which to differentiate between high fired and low fired porcelains, viz: such with Sillimanite being hard porcelains, and such without Sillimante being soft porcelains.

All the above investigation merely created in me a desire for personal observation of some of these interesting phenomena. I prepared slides from such porcelains as I was personally acquainted with, and although my ability to interpret the observations must necessarily be very meagre as compared with the work of others along this line, I offer to you my observations and conclusions in the hope that some light may be thrown on the practical side of this investigation.

From my observations, I conclude that porcelain consists of a matrix of fused spar and possibly other fluxes, with clay and flint suspended and more or less dissolved in it. If the heat has gone high enough, the degree of fusion may have reached the stage where we have a viscous glass in which is dissolved practically everything that enters into the compound; or if the other extreme is reached, we have nothing more than a conglomerate bonded together by a glassy substance made up of semi-molten feldspar, aided by any other fluxes present, and perhaps carrying small quantities of clay and flint in solution.

We know that the translucency is largely dependent on the alkalies, that the substitution of alkaline earths tends to produce stoniness, and also that the ratio of flux to clay to flint regulates the warping tendencies of the body produced.

What I desire to bring to your attention is the process by which these changes occur, and the extent to which the dissolving process is influenced by the addition of alkaline earths or the substitution of one alkali for another.

We cannot, at this time, cover the entire field, but I shall attempt to show you by the aid of the microscope and polarized light, what the relative action of a few different fluxes may be under given heat conditions.

For this study we will first look at porcelain marked "O," (Vol. X, Trans. A. C. S., page 266) which has the composition:

Feldspar	21.35
English China Clay	43.92
English Ball Clay	8.00
Flint	26.73
	100.00

We see here, standing out in bold lines, coarse granular matter, but on closer study we find that there are a great number of clusters of tiny needle crystals submerged in a liquid matrix, and the whole more or less obscured by a great number of tiny spherical particles through which light passes with difficulty. We also note numerous larger spherical bodies suspended in glassy matrix.

What may we assume these various materials to be?

We can safely assume that the finely ground feldspar has nearly, if not quite, reached the liquid state, since cone 12 was reached by all of the specimens here shown unless otherwise noted. The flint is the only other crystalline material introduced, hence I think we may safely assume that the majority of these angular coarse grains are particles of undissolved flint. We cannot hope to find the flint in true crystalline form, owing to the grinding process through which it has passed, but the strongest argument for my contention that these are particles of flint, lies in the fact that they display sharp angles and smooth faces, which we cannot expect to find either in the fused spar or the clay substance.

The tiny semi-opaque spheres, which cloud the matrix, are undoubtedly clay-substance, and the large spherical particles above referred to are undoubtedly gas bubbles, coated with the opaque clay substance. These gas bubbles

have almost clear surfaces where the fusion has progressed to a sufficient degree, but with feldspar alone as a flux and in the proportions of "O" porcelain, the gas bubbles are coated so heavily with undissolved clay substance that they are practically opaque.

We will now add to this "O" porcelain, two per cent of $CaCO_3$ as whiting by which we have "K" porcelain (Trans. A. C. S., Vol. X., page 267). Note the change in the appearance of the flint or quartz grains. The edges are no longer distinct, showing that the matrix has begun to attack and dissolve some of even these large particles of silica. Also note the lack of contrast between the matrix of fused spar and the clay substance. The spar matrix in porcelain "O" was nearly obscured by the substance while in porcelain "K" the addition of only two per cent of $CaCO_3$ has enabled the matrix to dissolve much of this clay substance. Also note the isolated clusters of needle-crystals where the fused spar matrix exists in large amounts.

We will now look at porcelain "L" (Trans. A. C. S., Vol. X, page 267), which contains two per cent of $CaCO_3$ in the form of pulverized marble. This should be similar to "K" porcelain, except that it will show any difference which may arise from the $MgCO_3$, of which the marble contains 17%. This we find to be true, except that the matrix is not quite so clear as is that of porcelain "K." This phenomenon may have some connection with the note in Vol. X. to the effect that "L" porcelain seemed whiter than "K" or "M" porcelains. This cloudiness is due entirely to the large amount of beautiful crystallite present, and which is very much more uniformly distributed than in "O" or "K" bodies. Note also that the masses of fused spar matrix are less distinctly outlined than in "K" body, indicating more fusion.

This notably increased number of needle crystals and the increase in size, and distinctness of same confirms the observation noted by Plenske that "an addition of magnesia gives more beautiful crystals".

We will next study "M" porcelain (Vol. X, page 267) in which the calcium is introduced as $CaSO_4$ or plaster of Paris. This porcelain is very similar to "O" body, indicating that the flux in this form is less active than when introduced either as whiting or marble dust.

Our next sample will be porcelain "P", which by Vol. X, Trans. A. C. S., page 98, you will find contains:

Genuine Cornwall Stone	43.69%
Whiting	.10%
English China Clay	34.00%
English Ball Clay	8.00%
Rock Flint	14.17%
	99.96%

This body is of the same formula as "K", "L" and "M" porcelains, but the introduction of Cornwall stone in place of feldspar has changed the percentage composition.

Note in this body we find a large number of patches of material similar to the matrix of "K", but which are fused almost to a degree equal to that displayed in "L" body. The crystal needles in "P" body are very large and distinct, but not so numerous as in "L" body. The line of contact between the flint particles and the fused matrix is clear and liquid-like. This is a peculiarity of the Cornwall stone, which we do not find in any feldspar porcelains, unless the feldspar has been previously fused.

We will compare the body just inspected with a body exactly duplicate, both in formula and in percentage composition, but in which the Cornwall stone is replaced by an artificial mixture of spar, clay, flint, magnesium oxide and fluorspar fused and ground. This body is known to you as porcelain "Q." (Trans. A. C. S., Vol. X, page 99.)

Porcelain "Q" seems very similar to "L" porcelain in formation, the matrix being almost entirely of clear fused glass which is exceptionally free from color or cloudiness. The crystals in this specimen are exceptionally large and

distinct, and seem to form a fringe projecting into the masses of fused matrix. Only when the mass of fused matrix is very small is its entire mass filled with crystal structure. I would note here, however, that the extreme clearness of the fused matrix in this body undoubtedly adds much to its ability to display its crystal structure, and evidently indicates almost a total solution of the clay substance. I also note the presence of an exceptional number of gas bubbles in this specimen.

We will now look at a specimen which I will call porcelain "S" and which is exactly identical with porcelain "K" except that it contains feldspar, which has been previously fused alone and reground. This "S" porcelain is fired at cone 10, whereas all previous specimens have been fired at cone 12. The crystals in this porcelain are small in number and only of moderate size and the flint particles appear to have been very perceptibly acted on by the fluxing action of the matrix. The matrix is similar to "O" in structure, indicating that at cone 10 this dissolving action of the matrix noted in "K" does not occur. We note, however, the same clusters of distinct bubbles that we noted in "Q" where the flux consisted partly of fused and reground spar.

We will next look at porcelain "U," cone 10 fire, which consists of the same materials as "K," except that the feldspar used is a softer spar. This body is explained in another paper read at this year's meeting, and is very similar to "O" body, but the matrix is clearer and the quartz grains are more attacked by the matrix than in "O." Note that the quartz grains are not surrounded by the clear area as in "Q" body, but that a cluster of semi-clear globules, as though the presence of the matrix at this temperature tended to only partly dissolve the opaque clay substance. The clay substance in the remainder of the matrix seems to have lost some of its opacity, although its cloudiness is still distinct.

We now come to the soda spar body, referred to in another paper read at this year's meeting. This is known

as porcelain "V," cone 10 fire, and is particularly interesting because it shows more effects of dissolving action than do any other of the samples shown. The clay substance is notably attacked by the matrix, being apparently completely dissolved by it. The quartz grains are very rounded, indicating partial solution. The most interesting point brought out by a study of this porcelain is that we find in it, at cone 10 firing, a very even distribution of large needle-like crystals.

Another peculiarity of this specimen is that there are bubbles or holes appearing in the body of the semi-dissolved quartz grains, indicating that the flint particles are beginning to actually dissolve, and the opacity of these flint particles indicates further the extent to which they have been acted on.

In order to study the progress of solution and crystallization with rise in temperature, I prepared a porcelain of the following composition and called it

"W" PORCELAIN.

Feldspar	33%
Flint	17%
American China Clay	25%
American Ball Clay	25%
	100%

This body was prepared in one mass and then divided into three portions which I had fired in a normal atmosphere at cones 9, 11, and 13.

NOTE — I have used only American Clays in this porcelain in order to compare it with the English Clays used in the other porcelains.

It contains no calcium and should show us the progress of vitrification and solutions and at the same time indicate at what temperature the Al_2O_3 SiO_2 crystal forms. The results of these three firings are all that could be hoped for in the matter of progressing solubility.

"W" Body. At cone 9 we have a more opaque cloud of clay substance than in "O" porcelain, while the exposed quartz grains are much sharper in outline, and with no appearance of corrosion. The clay substance globules in this body are practically opaque and so cloud the feldspar matrix that the tiny needle-crystals present are only dimly outlined. Needle crystals are, however, very evenly distributed, altho very small in size.

"W" Body. At cone 11 we note some improvement, the porcelain now being practically the same as porcelain "O" at cone 12. Isolated patches of distinct needle crystals are noted, altho the cloudiness of the matrix still prevents the smaller crystals from appearing distinct. At cone 13 we note a very pronounced change. The quartz grains appear clear and slightly corroded or dissolved on the edges. The feldspar matrix, however, is notably clearer and the bubbles suspended in it are almost absolutely free from cloudiness. I note in this body the larger clusters of clear bubbles similar to those noted in "Q" body. The feldspar matrix is very evenly filled with crystal needles of good size and distinct outline. The larger particles of feldspar, which in the two preceding specimens retained their general outline, are lost in this specimen, and their presence is only indicated by clusters of fine Sillimanite crystals.

I will now show you for comparison, a vitrified body fired at cone 10 and composed of flint and clay substance, and in which the feldspar is replaced by a fusible iron-bearing clay. Note how clear this matrix appears and also the presence of tiny crystal needles, which are evenly distributed throughout the entire mass. Also note how distinct the fine globules appear, indicating that this form of flux does not possess any great power as a solvent of clay substance. This is in direct variance with all regular porcelains in which we note that as the matrix becomes transparent, the clay substance disappears.

I also want to show you a specimen of bone-china. This was cut from a first class specimen showing fine surface and translucency, and no evidence of warping. Note the great amount of opaque material and the absence of anything that might be classed as crystalline. The calcium phosphate apparently does not exist in a crystalline form in this specimen, nor is there any apparent crystallization as a result of vitrification in this specimen.

SUMMARY.

As a result of this line of study, I offer you the following as my interpretation of the development, pyrochemically, of porcelain:

Of all the ingredients entering into the composition of the porcelain, the feldspar is the first to act. If it is a hard spar, cone 9 may be reached before it does more than bond together the other ingredients into a conglomerate mass. As the temperature rises, the feldspar becomes more active, dissolving first the clay substance and later the flint particles until at cone 10 the porcelain begins to show evidence of Sillimanite crystallization. At cone 13 a hard spar becomes completely fused, and is completely fluid permitting such complete crystallization as conditions and other ingredients will permit.

The substitution of a soft potash spar for a hard potash spar is a point worth noting. I find that a difference of two cones in the maturing temperature may be effected, and an equal amount of dissolving action obtained. A study of the relative analyses of the spars would lead one to suspect such a difference. This inclines me to the belief that the virtue of very hard spar lies largely in the fact that a longer, higher fire gives more uniformity of heat distribution. With equal care at lower temperature, a soft spar should give equal results and save considerable in fuel and kiln maintenance. The addition of some other flux, even in small quantity, causes the matrix to become

much more active as a solvent. Whiting and pulverized marble are more powerful in this respect than an equal equivalent of plaster of Paris, and they give to the matrix a dissolving power in excess of that obtained by an equal amount of flux in the form of feldspar.

The substitution of a soda spar for potash works a greater change than is possible in any other way. Besides causing the remarkable change in sounding quality, the soda spar gives to the matrix a dissolving power that is remarkable. As evidence of this I call your attention again to the splendid crystal formation which is noted in this specimen. No cone 12 specimen observed, has reached this stage, hence I assume the soda spar body reached a higher stage of solution at cone 10 than the other specimens reached at cone 12.

Regarding the Cornwall stone, the only note I make is that it acts more like a fritt than a spar, although its fluxing action is apparently not equal to that of a fritt of the same composition. In fact, the activity of this fritt in dissolving the flint particles is remarkable as compared to an unfritted flux. The advantage of fritting the spar and lime together, over that obtained by fritting the spar alone, is strikingly displayed in this study. A peculiarity of all bodies containing fritted material is, I note, that they display clusters of segregated bubbles which we only find elsewhere in the soda spar porcelain and in the porcelain containing 33% of feldspar and fired at cone 13.

This segregation of bubbles suggests to me that the matrix is ordinarily too viscous to permit of the gas passing off freely, so that the bubbles expand where they are given off. When fritted flux or soda spar is used, the matrix is sufficiently fluid to permit of the bubbles passing off more freely and the segregation occurs as noted.

In closing, I desire to add a note concerning the action of fluxes on the different clays.

From a study of mixtures of various clays with spar in the proportion of 70% clay and 30% spar, and fired at

cone 12 in a 40-hour burn, I find that the ball clays display notably less solubility in the fused feldspar than do the china clays, altho the ball clay porcelain displays by far the finer texture. I also note far greater crystalline development in the China clay than in the ball clay porcelains. This same phenomena has been noted by Zoellner in his table of kaolins and clays tested, in which you will note that the *Wildstein Ton* and the *Putschirn Ton* develop the least Sillimanite structure, and at the same time possess the greatest plasticity. This would lead one to infer that the ball clay exists in too large grains for ready dissolution or that it possesses some form of structure or some quality which retards the fluxing action of the molten feldspar.

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DISCUSSION.

Mr. Watts: I want to say, on concluding this paper, that I desire to acknowledge, through our *Transactions*, my indebtedness to the Bausch & Lomb people for their great generosity in furnishing the apparatus we are using; also to Mr. Fred Locke, who has given me repeated opportunities to use his high power microscope for my study of porcelain. I doubt if very much could have been accom-

plished were it not for his kindness in allowing me to use it. But little could have been done without the polarized light machine, although we might have obtained something of the kind, but it would have required a very large amount of detail work on each specimen.

Prof. Orton: I think this is one of the occasions where the member who stays at home and says he can get it all in the *Transactions,* gets fooled.

I move that the American Ceramic Society tender Bausch & Lomb a vote of thanks for equipping us with this magnificent piece of machinery, without which Mr. Watts could not have brought the slides illustrating this paper; also to Mr. Locke for his kindness in loaning Mr. Watts his microscope.

The motion was seconded by several and then put and carried unanimously.

On motion a vote of thanks was also extended to Mr. Watts for the work he had done.

A SIMPLE COST SYSTEM FOR USE IN A PLANT MAKING A LARGE VARIETY OF WARES.

BY

FRANK H. RIDDLE, Colorado Springs, Col.

In many small plants that manufacture specialties it is sometimes hard to keep certain departments or men employed steadily on one class of work or specialty. It is necessary to shift about from one job to another, although it may be the same sort of work. This shifting about makes it hard to keep accurate costs unless very careful records are kept. The writer has had this to contend with for the past eighteen months and has arranged the following system which, although far from perfect, gives quite accurate results without making the system so complicated that it is a cause of delay or extra expense.

I wish to state here that Mr. Mayer's article, Vol. II, page 161, was used as a guide in a good many cases.

It is the aim of the system to give an accurate account from day to day of the amount of work done and the cost of doing it for each department. This requires several steps, as follows: Daily record, department record, daily job record, total job record, and ledger record.

The daily record is given out to each employe every morning and is filled in as follows:

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DAILY RECORD

DEPT. Pressing & Moulds

NAME John Smith | DATE Dec. 28, '08

	Hrs.	Min.
Pressed Center Piece - Job 121		90
Pressed 16 panel tiles - Job 121	3	45
53 lbs Clay used.		
Made 5 double tile moulds - Job 121	1	15
45 lbs plaster required		

All state the work done and the material required. In casting, where there are some hundred shapes, it would be tedious and unnecessary to put down each design number. In this case the caster states the number of small, medium and large pieces cast. In putting on handles and similar work the design numbers, etc., are stated. There are many things of this sort that come up that would have to be settled differently for every plant.

In all records the amount of material required for unusual or varying work is stated. In making stock tile and regular work of this sort the exact amount of clay required has been determined previously and a tabulated record kept, so that it is unnecessary to state this each day. In casting it would be difficult to give the amount of slip used, so this is kept by the month and charged for that period of time.

The daily records are collected and entries made in the department records and daily job records. For example, take the daily record shown:

The first item, pressing center piece, Job. 121, 1-2 hr., would be entered in the department record for Pressing

and on the Daily Job Record for Job 121. Of course, all pressing done that day would be entered the same and any work on Job 121, whether pressing, finishing, glazing, or anything else would be entered on Daily Job Record for Job 121.

The Daily Job Record used is as shown:

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SHOP ORDER NO._____

FOR { STOCK_____ DATE ORDER REC'D_____
Special Order_____ Date To Be Completed_____

JOB NO. 121

Date			Number	Time	Amount	
Dec	23	Pressed center piece	3	1/2		13
		16 panel tiles	3	3 3/4		93
		53 lbs clay				21
		5 double tile moulds	3	4 1/4	1	06
		45 lbs plaster				45
		3 Moulds	1	2		85
		20 lbs plaster				20

These records which are kept in the shop or manufacturing office show the order, whom for, when taken, when to be finished, the time certain work was done, the material required, the workman's number, time required and cost.

The department records are ruled in the usual manner, as follows:

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PRESSING RECORD

DATE			TIME	NO.	COST	
Dec	28	Centerpiece for job 121	1/2	3	$	13
		16 panel tiles	3 3/4	3		93
		53 lbs clay				21

Giving the date, work done, time, workman, and cost. The material used and the cost of it are also entered here. The cost of the material is determined by the cost of making clay or preparing any other material in the previous months and will be described later. At the end of the month the department records are footed and posted in the Ledger Record. This gives each department the matrial used, amount of work done, and the cost of doing it, including cost of power. In dry pressed tile, for example, the records would read:

10,000 6 x 6 tile, 42 days (8 hr. days).....$ 60.00
15,000 pounds of clay 73.65

Total cost of pressing and clay.....$133.65
or $13.36 per 1000

If a man has to do any small repair work to his press, sweep out, go out after oil, or any other thing which takes him from the press or actual manufacture, this work is included just as the actual pressing, so that absolutely everything done in that department is charged to the tile pressed. In this way running along for several months and comparing cost it is quite easy to get absolute cost of

any stock or job work. One place where this does not hold good is in the burning. Here another system is required.

The daily records and the kiln department records are the same. Determining the kiln cost and the charging of this are somewhat different, however. The department record shows every bit of work done on one kiln from the time it was set until drawn, cleared up, and ready for the next setting.

The materials used are also shown. Record shown as follows:

Setting	$23.86
Firing	11.38
Drawing	5.90
Sorting	1.45
Coal	30.00
Cones	1.60
Stilts	.50
Wads	.40
Light	2.00
Breakage of saggers	2.63
Total cost	$79.72

This gives exact cost but does not tell how to charge up the various jobs that may be fired. This is done as follows: The saggers used are named according to size and shape and if a big oval is filled with ware for job 121 it is marked by the kilnman as shown. Again stock tile, in 10 square-tile sagger, as follows:

SAGGER RECORD KILN I FIRING NO. 40

10 Sq. Tile	Big Oval	Small Oval	14 in. Oval						
Job 121	Job 121								

This gives an exact record of what each sagger contains. The volume of each sagger in square inches is known and then the square inches of space for each job readily found. This cost has already been found for the total volume so that the cost of each job can be readily determined by proportion.

This method seems and is rather tedious in a way, but several methods were tried and this proved best. If record is taken in setting, it causes less confusion than in drawing and is more accurate as the ware going in is all properly marked and mistakes avoided, etc. The loss must be taken and the marketable ware made to pay the way of culls in order to get at the absolute cost. All saggers broken during loading, firing, and setting are charged up to the kiln and divided equally per cubic inch, so that this is taken care of. The cost of saggers is obtained from the sagger record.

Now, if the kiln cost $70.00 for firing and job 121 required 25% of the space, then the firing of job 121 on the Job Record would be charged 1/4 of $70.00 or $17.50. Glazing, etc., is all done the same way. When a job is complete the various items on it are collected for departments and entered on the total Job Record, as follows:

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SHOP ORDER NO. ..... **JOB NO.** 121

Date Order Received ..... **Date To Be Completed** ....

FOR { **STOCK** .....
SPECIAL ORDER Mantel for Ten Bonfiles of Denver

	AMOUNT
CONTRACTING	$1 00
DRAFTING	90
MODELING	2 32
MOULDS	14 21
PRESSING	10 55+
CLAY	1 75-
PLASTER	3 19
GLAZE	(2 6)
BISCUIT-FIRE	1 25-
GLAZING	9 36
GLOST FIRE	11 80
FINISHING	2 65-
MISC. – Packing	2 30
Total	$61 28+

Cost of glaze

This total job record and department ledger records are taken into the business office and filed for reference, so that at any time the exact cost can be determined.

Of course, in here it is necessary to determine the percentage of burden expense, to be added to each piece of work and, on the job records, the profit. This gives the final price which should be asked for the ware. This is done as follows:

The voucher system is employed and at the end of each month every expense of the plant is vouchered and distributed on the back of vouchers and entered in the proper column of the voucher record. The columns are as follows:

Burden Expenses.	Cost Expense.	Investment.
Advertising	Manufacture	Plant and Kilns, actual new equipment, not renewals.
General expense	Light for kiln and power	
Int., Taxes, Ins.	Part of M't'ls. & Sup.	
Light (all but kiln light) and heat	Moulds	
Mach. and Renewals	Saggers	
Office	Shipping and Packing	
Miscellaneous		
Part of M't'ls. & Sup.		

If the necessary expense equals 100% it is very easy to calculate the burden per cent and add it to the actual cost of making to get the real cost. Then the per cent profit is added on to get the selling price.

If the contracting department estimate sheets are itemized properly, it is very easy to compare the estimate and the actual cost and find out where any mistakes were made and how they should be corrected in later quotations.

All drawings and specifications for work done are filed for comparison with any new work arising, so that the system not only gives accurate costs and chance for

comparison, but also specific data for reference at any time when unusual jobs come up which can not be estimated by square foot, volume, weight, or some other similar method.

Another thing done is the listing of all ware going to the stock house at net selling price. If the net total for the month is not greater than the total expenses for that time, it shows immediately that goods are being sold too cheaply and that the manufacture must either be improved and cost lessened or else selling price raised.

A few words about the obtaining of the cost of materials prepared at the plant may be of assistance.

First a power log is kept. This record shows the number of hours each machine has run for the month. The power required for each machine is known, so that it is very easy to determine the number of horse power hours each machine has as above used.

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POWER

DATE		Motor	TIME	WORK DONE
Dec	17	I	8 A.M. - 4.45 P.M.	Acid Camp-Filter Pump, Mat'l Pan, Dust mill
		III	7 " - 3 "	Glaze Mill.
		V	9 " - 11 "	Grinding Wheel.

The actual cost of the total power is determined by the bill rendered each month by the electric company for power used and the regular daily record reports for labor. This total is then divided proportionately for each machine, so that it is possible to know the exact cost for running each machine. The daily records show the amount

of clay or other material treated at each machine and the total cost is equal to the power, labor, and cost of the raw material. Of course, in washing clay the percentage of knockings must be known and taken into account. A check is obtained by keeping a record of raw material used for the month and the prepared material ready for manufacture. From this it is very easy to determine the cost of any material for a given quantity and then charge the manufacturing up with the material as it uses it. Some months a sufficient quantity of one material will be prepared to last several months and by this means this material is not charged as being used in that month, but as it is actually used.

These methods contain many defects but they are so small in the long run that the expense of correcting them and the extra daily work required would be greater. It might be interesting to know that the keeping of the initial cost system actually costs $10.00 a month.

DISCUSSION.

Mr. Watts: In starting the discussion of this paper, which is a matter of dollars and cents, I want to ask Mr. Riddle if I understood him correctly, that he prorated the overhead on the basis of the direct charge; in other words, did you prorate your undistributed expense of the business from the amount actually chargeable against the job, or did you figure it from the amount of material put into it? For instance, if you had ten jobs at one hundred dollars each in direct charge, that would total up one thousand dollars; and if you found you had spent five hundred in overhead expenses, would you prorate that over the ten jobs, as five hundred is to a thousand?

Mr. Riddle: Ordinarily you would, but if your observation showed you you had expended more on one job than on another, you would add to it. That is where the system is weak, and judgment has to be relied on.

Mr. Watts: We have spent a good deal of time on the cost question at Victor. I would say, to its credit, that there is a very small amount of capital expended which is not a direct charge on the particular article for which it is used. Of course, light, heat, power and office help generally, aside from the maintenance of the selling department, are each charged or prorated directly and are all charged against the piece of work being done, so that there is a very small amount of "overhead." I would say that there we prorate our overhead undistributed expense and add it to the direct or actual charge against every individual piece of work. If in making a certain insulator, we find we have spent ten thousand dollars and only eight thousand is a direct charge, we have an overhead of twenty-five per cent to be added to every insulator. If there is additional engineering to be done upon some insulator, it is charged to that particular insulator, so there is very little undistributed investment.

Mr. Barringer: Why does the item of clay have to be carried through on each of your blanks?

Mr. Riddle: You have got to know from the man himself how much clay he used.

Mr. Barringer: You base it upon the weight of the pressed objects?

Mr. Riddle: Yes.

Mr. Barringer: Did you ever base it upon the unit of the fired ware; the weight of the biscuit—the fired weight?

Mr. Riddle: We never have.

Mr. Barringer: In that way you can get the cost at the end instead of the beginning. You can always find out what the unit of the clay used, cost.

Mr. Riddle: We hardly think it necessary to find the monthly cost of the clay; but where you charge it to the different jobs direct and use different clays, I think you would have to put that in separately.

Mr. Barringer: If you knew what a pound of clay cost, you would simply find it by that, wouldn't you? Take a certain amount of clay and it cost so much; pug it and fire it and dry it and you figure how much you lose by driving out the water in the drying and burning; and thus you get a figure which shows what a certain amount of clay cost, in any shape.

Mr. Riddle: You would have to include whether it was a piece of thin ware or a thicker ware or what it was.

Mr. Barringer: We have two kinds — the dry process and the wet process—in porcelain. We know what a pound of dry process clay costs and what a pound of wet clay costs; whatever that weighs we simply put the figure upon it. That is the actual clay and, no matter what you do with it, it cost that much.

Mr. Stephani: We get our prices, as Mr. Barringer says. After it is burned we know the percentage of the loss in water and we know their cost, thus we get the cost of the clay. In terra cotta you couldn't weigh the separate pieces very well.

Mr. Riddle: That certainly seems a very good plan and I will think it over.

Mr. Simcoe: I would like to ask Mr. Riddle about the saggers. You have a special type; do you charge them up to that particular job or run the saggers constantly and keep them charged up with the kilns?

Mr. Riddle: That is a part of the kilns. If broken we charge it to the burning. That is a part of the system, but the system has not been run long enough to tell absolutely how successful this is. Of course, if we have some unusual job, which requires special saggers to be made, these saggers are charged directly to the job for which they are used.

Mr. Child: I would like to ask if you can bring a balance on each kiln as soon as completed?

Mr. Riddle: Yes, sir.

Mr. Child: I have been trying to work out a cost system for a drain tile plant. I have not been able to balance the kilns except by the month, because the number on fire at one time may vary from day to day. The only way I have been able to do is to take the total cost for burning during the month and divide by the number of kilns burned.

Mr. Riddle: You have a large plant; we have a small plant. What I meant by saying we can get at the balance is, we can get a balance of the entire cost per kiln and can charge it up. You can see what I mean.

Mr. Child: Do you figure your percentage of loss on each kiln?

Mr. Riddle: Yes. The amount is known of what goes in and what is good when it comes out. The culls are broken up right away. Supposing you had a thousand pieces in the kiln and only nine hundred came out good, you have to charge the 10% loss up to the 90% saleable ware. If you got only a hundred out, it would be very expensive.

Mr. Watts: I would like to say, in that connection, that in our experience only an average of a number of months will give you very definite knowledge. Take a number of months or a year and average up the cost and results of the burning. You have to do that on a great many kilns to make the data really valuable. As Mr. Child has said, the cost of one kiln today and three tomorrow will make your firing cost vary from day to day and it would hardly seem to me satisfactory at all unless you took an average, if each varied.

Mr. Porter: In regard to the matter of moulds; I see it is charged up in the cost. Don't you have some salvage?

Mr. Riddle: This is upon a particular job. We get an order and it will say, "Moulds to be destroyed." The architect when giving the order specifies that when completed the moulds are to be destroyed.

In regular stock ware it is decided how many pieces will be made from a mould and the cost of this would be divided up among the pieces made from it. There is an opening for error because you may not make the number of pieces, or the piece will not sell well and you have to stop running it before the calculated number has been made.

Mr. Porter: Is there any charge for saggers unless destroyed?

Mr. Riddle: No, sir. Excepting where there are special saggers made for some special job. If you make just sufficient new saggers to keep the stock up this method is all right. However, if you are increasing your supply of saggers at a greater rate than the breakage requires, this asset has to be treated the same as a stock of any other material, as clay, coal, etc.

THE LIFE OF A SAGGER.

BY

GEORGE SIMCOE, Northeast, Md.

The rapid growth of our sagger shord, or scrap pile, led to an investigation of some of the practical features of sagger manufacture, such as the various methods

The above cut shows some of the results

of manufacture, their relative cost and proportionate loss. This being a purely mechanical test we assumed our sagger *body* to be all right for the temperature and treatment it receives under our conditions, i. e., cone 12 to 13, maximum temperature, and rough handling by unskilled labor-

ers, in and out of the kilns, and when placed in bungs, no wad clay used at all to equalize the load on the rim of the sagger; and finally, owing to the fact that our ware is only fired once, the smallest point of support is left unglazed and consequently we have a weight of from 15 to 30 lbs. supported on an unglazed portion from 2 inches to 5 inches diameter, resting on a sagger bottom from 15 inches to 25 inches diameter. The results of this concentration of weight upon such a small supporting area is obvious.

The sagger body used is as follows:

33⅓% (by volume) Ostrander White Clay (from Ostrander, N. J.).

33⅓% (by volume) No. 7 Tennessee Ball Clay (from Whitlock, Tenn.).

33⅓% (by volume) Grog (produced by a mix of above).

The preparation of this body consists in grinding and mixing in a dry pan, followed by wetting down and ageing. From the ageing floor it is put through an ordinary horizontal pug mill to supply the demands of the sagger makers.

I thought it would be interesting to see just what proportions of the different sized grains our grog would contain, as we use it all, coarse and fine, just as it comes from the dry pan. I used a 20-lb. sample for the test; the following is the record of same:

10.0%—left on 4-mesh screen.
20.0%—passed through 4-mesh and left on 6-mesh.
15.0%—passed through 6-mesh and left on 8-mesh.
12.5%—passed through 8-mesh and left on 12-mesh.
18.5%—passed through 12-mesh and left on 40-mesh.
12.5%—passed through 40-mesh and left on 80-mesh.
10.0%—passed through 80-mesh and left on 120-mesh.
1.2%—passed through 120-mesh.

99.7%

Prof. Binns brought up the subject of saggers for discussion at a previous meeting, in the course of which, Mr. Ernest Mayer gave his experience and pointed out the help derived from an article on the subject of Saggers in Mr. Karl Langenbeck's "Chemistry of Pottery" and recommended that a potter would do well to consult this article when difficulties in the sagger mix arose.

At another meeting Mr. Barringer gave us some very interesting data on the supporting strength of certain clay mixes at cone 11, and other papers have been read that thrashed out the effect of varying the size of grog in refractory mixes and showing the different results therefrom. And so you see that it is more from a pyrochemical standpoint that the *sagger* has been dealt with.

It will be my endeavor to set forth as near as possible what is the *cheapest* method of making *saggers* for our particular conditions.

First, let us enumerate and describe briefly the various methods employed in manufacturing saggers:

1st—By hand.

2nd.—Jiggered.

3rd—Pressed by machine—Power may be either hand, pneumatic or steam.

4th—Rings made on sewer pipe machine—bottoms, which are separate, made by hand.

5th. Made under high pressure from slip in a two-part plaster-lined casting.

1st—*By Hand*—Familiar to all potters, using a drum to form sides from strips cut from clay that has been batted down to uniform thickness and the bottom, which is also batted down in an iron ring, to give it proper form and thickness. Ring and bottom thus made are welded together by hand. This method has two important advantages, viz: the making of all sorts of irregular shapes and the use of clay having low per cent water content.

2nd—*Jiggered*—Jiggering saggers is somewhat of a departure and can hardly be used in making any but the

round saggers. As we use the round sagger *entirely,* we make all of our saggers by this process. A description of this method is as follows:

A good heavy jigger is used, such as crucible manufacturers use in making their largest sizes. Instead of a cup a face plate of sufficient diameter and strength is screwed on to the head or thread at the top of spindle. Cast iron rings are made of various diameters to form the sides of the different saggers. The inner surface, top and bottom of these rings are machined true and smooth. At the bottom of the ring is a ¼ inch flange extending outward; four dogs placed concentrically upon the face plate, clinch the flange and hold the sagger in place. One of the dogs is keyed in so that by removing it the flange of the ring may be slid from under the other three. Ordinary butchers' paper is used to keep the sagger clay from adhering to the sides and bottom.

By this process one man can make and carry away 150 to 175 saggers, 20½ x 7½. We give him 2c each for such saggers. This process has cheapness to recommend it and speed, but, as in all cases where you pay by the piece, carelessness, etc., will run your cost up. The clay used in this method is rather high in water.

3rd—*Pressed by Machine*—This is a very simple operation, consisting of the placing of the bat upon one or the other die of the machine and applying the power, whatever it may be, and the dies press the clay into shape. When the dies are raised you remove the finished sagger. The clay used is relatively low in water. To operate these presses it requires from 2 to 3 men to develop any speed; three men would hardly make 100 per day of the type sagger described in the 2nd heading. This process has the advantage, however, of being able to make most any shaped sagger, which for that class of work gives it a great advantage over the hand made. Permit me to quote the *Clay-Worker,* taken from a clipping from the *Sprechsaal,* No. 13, 1908.

"Presses for the manufacturing of saggers have proven a great success. Four-corner saggers, such as are used in whiteware potteries, are made very nicely on such presses, and the saggers have proven that they will stand the fire better than the hand-made ones. A convenient size is 20 x 14 x 12 inch. The body should be properly made in order to press good. A reasonably short body will give better results than a fat body. The drying should be done slower than for turned or hand-made saggers. An addition of fine coal slack or saw dust to the mix will be advantageous in order to get a body which will stand rapid heating and cooling. The labor and the general cost of the manufacturing of saggers by machine will come to about one-quarter of the cost of hand-made saggers."

4th—*Rings made on a sewer pipe machine and bottoms made by hand.*

The clay for these rings was shipped dry-ground to the plant where the experiment was performed, 1500 lbs. for a batch, and tempered in their wet pan; a pipe of the desired diameter and thickness was run out and cut off into rings the desired length and smoothed and sponged; they were given their first burn in a sewer-pipe kiln so as to harden them for shipment; bottoms were made by hand to fit these rings. In addition to the sewer-pipe rings, I had some rings jiggered. If I could have had a large size vertical auger tile machine I would have made a check test with it, but it was not available at the time.

The table which will be shown later will give an idea of how short was the life of such saggers, but the unusually short life of the sewer-pipe rings may have been due to two controllable causes: In having the clay shipped, it was mixed in thirds by weight and not by volume, and further, the rings were not as level as could be made. I believe that the loss was due chiefly to the latter cause, as the jiggered rings which were much smoother, lasted much better. The expense of such a process could not be based on the figures I have; in fact, all that I can show for these

methods is against their use, but I have faith in the scheme that if not the ring-slab sagger, a welded complete sagger could be made very cheaply by the use of rings made on a vertical tile machine. By means of an endless belt the rings could be conveyed where bottoms (hand-made or cut out of a flattened section of ring) could be welded on. Such a process is at present used for making large crocks, 60 to 100 gallons.

5th—*Made from slip in a plaster-lined cast-iron mould* This method I shall but touch upon, as in this country it is very little known, though abroad they make glass pots in this manner very satisfactorily; if glass pots, why not saggers? We did not feel that we could afford to investigate along this line. The greatest expense of this process would be the necessary castings, as quite a number of each size would be required, if speed was desired.

TESTS.

In order to make some comparative tests as to the life of saggers made by the above processes, the following outline was arranged, but only partly carried out, owing to various business conditions. In making this outline we had to bear in mind expense, and only on our standard No. 35 Sagger (20½ x 7½—round) made by jiggering, could we get anything like a good test. In all the other tests we took a size and shape that was as near being comparable with this size as possible and for brevity's sake will consider all tests equal in so far as size may be considered.

1st.—*Hand-made Saggers*—15.6% water. Made 11—No tare drying and to kilns.

Fire	Good	Tare	Content
1st	11	0	Empty
2nd	10	1	7 pieces to a sagger, total weight 42 lbs. per S.
3rd	8	2	do

Test not continued.

2nd.—*Jiggered*—21.5% water. Made 150—No tare drying and to kilns.

Fire	Good	Tare	Content
1st	149	1	
2nd	140	9	1 pc. to a sag. wt. of same 11½ lbs.
3rd	121	19	do.
4th	108	13	do.
5th	80	28	do.
6th	64	16	do.
7th	55	9	do.
8th	51	4	
9th	39	12	
10th	22	17	
11th	14*	8	

*Not safe for anything but covers.

3rd.—*Pressed by machine*—Hand-power—15% water.

Fire	Good	Tare	Content
1st	4	0	Empty
2nd	4	0	49 lbs. supported by 2 3/16″ diam. surface
3rd	4	0	60 lbs. supported by 3″ diam. surface
4th	4	0	60 lbs. supported by 3″ diam. surface
5th	4*	0	60 lbs. supported by 3″ diam. surface

*Still look good.

4th—*Rings made on sewer-pipe machine and bottoms made by hand.* Both 15% water.

(a) Made 21 *Rings*—No tare. Made 22 *Bottoms*—No tare.

Good	Tare	Fire	Content	Good	Tare
21	0	1st	Empty	22	0
8	13	2nd	11½ lbs. each	20	2
0	8	3rd	11½ lbs. each	3	6

4th.—*Using special jiggered ring and hand-made bottom.* Ring—10% water. Bottom—15% water.

(b) Made 14 *Rings*—No tare. Made 16 *Bottoms*—No tare.

Good	Tare	Fire	Content	Good	Tare
14	0	1st	Empty	16	0
14	0	2nd	11½ lbs. each	16	0
12	2	3rd	11½ lbs. each	15	1
10	2	4th	11½ lbs. each	11	2
9	1	5th	11½ lbs. each	10	1
8	1	6th	11½ lbs. each	10	0

5th.—*Made from clay slip* under high pressure in two-part cast-iron dies lined with plaster.

No test made owing to lack of samples.

In the foregoing tables I have purposely avoided showing tare by per cent as the figures would be misleading, owing to the wide variation in quantity; however, they help furnish sufficient data for the drawing of some conclusions.

CONCLUSIONS.

1st.—For a plant using round jiggers entirely, the 2nd method, viz., jiggered, seems to be the best when considered from the standpoints of economy, speed in making, etc. The sagger machine costs from $200.00 to $300.00.

2nd.—Where it is necessary to have irregular shapes and round saggers, the 3rd process or power press is good and can be used to make all of the shapes, but if there is a demand for a fair proportion of round saggers, it might be well to use a jigger machine in connection with the press. A press costs from $300.00 to $600.00, depending upon size and kind of power applied.

3rd—The 4th process is interesting enough to warrant further investigation, owing to the division of weight in handling at kiln and further, cracks which are developed in one part are not transmitted to the other, so that if a ring is broken you have the bottom, and vice versa. A good outfit for making could be constructed within $3 00.00.

4th.—The first, or hand-made process, has little to recommend it save that of long usage and a probable belief that the only way to make a glost kiln stilt sagger was by this process. In fact, however, the jiggered sagger can be made for glost kiln service with satisfaction and at reduced cost—this also applies to the 3rd, or power press.

5th.—As a final word I would like to recommend to the *engineers* of this Society the devising of some practical and economical scheme to make saggers from slip by high pressure.

DISCUSSION.

Mr. Stover: As soon as I found out that this sagger machine was working in our city I wanted to see it. Mr. Crossley invited me to witness its workings, as the first man who made them. I found that they had put in three laborers at $1.50 per day; that it had been running for three weeks; and I found they were running off over five hundred in an eight-hour day, and I have since learned they have made a thousand.

Mr. Watts: How large a sagger were they making?

Mr. Stover: I think the one they were making was 14 inches round x 7 inches deep, and making some square ones for electric porcelain.

Mr. Watts: You will find when making a twenty-inch sagger you won't make over one-quarter of that with the same number of men.

Mr. Stover: I understand they are now making a larger machine and making saggers for sanitary work.

Mr. Elcod: Has anybody had any experience in making saggers of carborundum or corundum?

The life of a sagger, made out of plastic clay, fire clay and grog, — is very limited, as we know. And it seems to me, that some day, saggers will be made of materials, which will be of much superior quality as regards resisting the fire and the sudden changes of temperature; — and which will withstand an indefinite number of firings, — unless broken by a mechanical force. Six or seven years ago, I made some experiments on these lines, in the Seger laboratory, Berlin. I used corundum, — which is made chiefly out of bauxite. I took different

grades of corundum and mixed them together with about 5/8% of a plastic stoneware clay slip. I cast some vessels out of this mixture and fired them. I took these vessels, and heated them repeatedly up to white heat — threw them in cold water each time — without being able, even to crack them.

I made similar trials in this country with carborundum — which acted the same.

At that time I thought to make cooking vessels out of these mixtures, which looked to me ideal, for such a purpose. One could line the inside of the vessel with a mixture of some kind, to be white and vitreous and glazed on top of that — inside only. I made some trial saggers, in this country, using carborundum in the mixture and in other cases I lined only the outside of the sagger with it thickly. But I am sorry to say, I have no final results to put here before you. But at the same time I can assure you that either carborundum or corundum — will make an ideal sagger. To start with, it is quite an investment, as long as these materials cost so much more than common fire clay;— but they hold their values in any shapes, and can be used over and over again.

Mr. Watts: Did you make any observations on the point of the strength displayed, the nature of the article and whether it was capable of supporting a considerable weight?

Mr. Elcod: No sir; not by itself, unless it is fired in an electrical furnace, up to their softening point — which will be impracticable today. I have used a very plastic stoneware clay, such as English Ball Clay, as a binder, and I am convinced that such mixture will withstand the weight — which saggers have to withstand in our pottery kilns — especially if they are pressed by a hydraulic press.

Mr. Foley: I would ask Mr. Simcoe in what condition the clay is worked on a press; do you use it as a dry dust, or how?

Mr. Simcoe: It has a fair amount of water in it, just enough to make it run a little.

Mr. Foley: And you use oil to oil the pot?

Mr. Watts: We don't soak the plunger and die.

Mr. Foley: We always put an oil on the clay.

Mr. Jackson: I would like to ask the gentleman what he thinks of the sagger press; what seems to be the general opinion of saggers made by a press for pottery purposes?

Mr. Stover: I asked that question and they answered me they lasted about as well as the hand-made.

Mr. Jackson: Mr. Simcoe's proposition is quite different. The strain is all down and the temperature varies.

Mr. Price: In regard to saggers: Last fall we found ourselves embarrassed by shortage in saggers and large orders to be filled. The sagger maker did not seem to be able to catch up. We installed a sagger press and have not been troubled since. It was the Crossley type, making one hundred per hour and requiring two boys and one man to operate. Material, stiff clay mixed half and half with grog — local clays. The life of the sagger increased from three to five firings and burned at cone No. 12. The size of the sagger was 14 inches x 10 inches x 9 inches.

We found the uniformity of pressed saggers enabled us to set out a kiln to better advantage, partially eliminating wads.

The two dies were well oiled. In view of the tendency for bottoms to drop it was proposed to set the green sagger while drying upon a coned plaster slab, thus giving a slight inward rounding to the sagger. It remains a matter of doubt whether this is of sufficient value.

In regard to carborundum or corundum, I would like to hear more. It seems that the inherent physical quality of same would render such use impracticable.

Mr. Barringer: I wish to present a rough description of the machine used by the General Electric Company at Schenectady, for making saggers for the burning of electrical porcelain. This machine is of the same general type

as the flower-pot machine. The lower die conforms to the shape of the outside of the sagger while the upper die is made to give the shape of the inside of the sagger. The saggers used for electrical porcelain are mostly round saggers 12 inches in diameter and varying in height from 3 inches to 10 inches. The sagger body consists of equal parts, by volume, of fire-clay and coarse grog. The operation of shaping the sagger on the machine is very simple: The lump of clay to be shaped is placed in the lower die and the lower die is then raised by hydraulic pressure to meet the upper part of the die, which revolves but is fixed vertically. This upper revolving part is driven by a motor placed on the top of the machine. As the upper and lower parts of the die come together the clay is squeezed between them and flows out until the space corresponding to the shape of the sagger is completely filled. The revolving part of the die presses the clay in all directions so that it fills the die uniformly and completely. With machine-made saggers we find that they do not go to pieces quite as readily as in the case of hand-made saggers. It was a very common experience with us, when using hand-made saggers, to have the rim separate entirely from the bottom after one or two firings, or to have the rim of the sagger split from top to bottom at the point where the ends of the slab of clay, which had been used to form the side of the sagger, had been joined. In order to use the hand-made saggers as long as possible we resorted to cementing the parts together, or tying them, so that they could be put in the kiln. With the machine-made saggers the breakage is not as sudden nor as marked in any particular place as with the hand-made saggers.

The average life of our saggers is six (6) firings. The machine referred to can turn out from 1500 to 1800 small saggers per day.

Mr. Binns: Do you use wads between the stacking?

Mr. Barringer: Yes.

A STUDY OF CHROMIUM TIN PINKS.

BY

ROSS C. PURDY AND GEORGE H. BROWN, Columbus, Ohio.

INTRODUCTION.

A complete study of the subject of chromium-tin pinks would involve a very large amount of experimental work, and hence, owing to the limited amount of time available, it was decided to confine the present investigation to one fundamental portion of the subject, working it out in as much detail as was deemed possible.

As generally understood, chromium-tin pink color is produced by a mixture of a chromium compound, oxide of tin, and a calcium compound, calcined and used as a colorant in a glaze. Depending on the (1) composition of the stain, (2) composition of the glaze, and (3) materials used in the stain, the resulting color ranges from pinks to dark reds, inclusive of all shades.

A brief review of published articles revealed the following points on which differences of opinion were expressed:

(1) *Source of chromium best suited for the production of the chromium-tin color:* Seger and Carter used acid potassium chromate, commonly referred to as potassium dichromate ($K_2Cr_2O_7$)—and Hull used chromic acid (CrO_3). Purdy used various compounds of chromium and stated that different results are obtained with different chromium compounds.

(2) *Influence of calcium on the chrome-tin color:* Seger found that if the lime is decreased, the color tends toward lilac, and if excluded, toward pink. Hull varied his lime from 0 equivalents to 6.25 equivalents on a basis of 1 equivalent of SnO_2, but made only five stains between the two limits. He did not secure the information desired. Hensel found that a reduction of lime weakened the color.

SCOPE OF PRESENT WORK.

As a result of differences of opinion on these points, it was decided that the present investigation should be designed to show:

(1) The effect on the pink color of the introduction in the stain of the chromium.

(a) In various combinations.

(b) In different amounts.

(2) The effect on the pink color of calcium when introduced into the stains:

(a) In varying amounts.

(b) As a carbonate.

As a guide in establishing the limits of variation, formulae of pink stains known to be in use commercially were reduced to a molecular basis with SnO_2 unity. These are shown in the following table:

TABLE I.

Molecular Formula of Commercial Chromium-Tin Pink Stains.

	CaO	PbO	KNaO	SnO_2	Cr_2O_3	SiO_2	
1.	1.127	.....	0.22	1.00	.0218	0.437	Fine Blood Red
2.	2.00	0.058	.....	1.00	0.029	3.33	Bight Red
3.	0.888	0.031	.....	1.00	0.0155	1.00	Fine Red
*4.	3.6	.....	.....	1.00	0.0091	0.893	Fine Red
5.	0.744	.....	0.062	1.00	0.0306	0.893	Brownish. Poorly Disseminated
*6.	0.800	.....	.....	1.00	0.0190	.....	Deep Red
7.	0.88	0.017	.....	1.00	0.0086	0.922	Brick Red
8.	0.864	0.015	0.0844	1.00	0.115	0.979	Dark Brick Red
9.	0.864	0.013	0.008	1.00	0.066	0.978	Pink

*All formulae here given are those of stains, except 4 and 6. In those two cases, all glaze ingredients were fritted and the whole applied as a single fritt. Only the proportion of CaO, SnO_2, Cr_2O_3 and SiO_2 are given. These two glazes contained other oxides.

It was noted in the above formulae that:

(1) The equivalent of Cr_2O_3 varies from 0.0091 to 0.0155.

(2) The CaO varies from 0.744 to 3.6 equivalents.

(3) The SiO_2 varies from 0.437 to 3.33 equivalents in the extreme, but approximates 1.0 equivalent in most cases.

(4) Lead oxide is present in five of the stains.

(5) KNaO is present in four.

LIMITATIONS AND CONDITIONS ADOPTED.

(1) All stains shall contain 1.0 equivalent each of SnO_2 and SiO_2.

(2) The Cr_2O_3 and CaO equivalents shall vary.

(3) The chromium shall be derived from:

(a) Green oxide (Cr_2O_3).

(b) Lead chromate ($PbCrO_4$).

(c) Potassium dichromate ($K_2Cr_2O_7$).

(4) The stains shall not be melted, but merely calcined.

(5) The stains shall not be washed or re-calcined.

(6) The same glaze shall be used throughout.

(7) Each glaze shall contain 0.1 equivalent of stain, thus introducing 0.1 equivalent of SnO_2.

THE STAINS.

Composition: In the following charts are given the molecular formulae, batch formulae and combining weights of the stains.

Constituents common to all stains but not given in the tables:

1 Equiv. oxide of tin.....149

1 Equiv. flint 60

CHART I.

Showing Molecular and Batch Formula, and Combining Weight for Stains in

Group A.

OXIDE OF CHROMIUM.

Eqv. Cr_2O_3	Eqv. CaO. 3.0	2.50	2.00	1.50	1.00	0.50	
0.001	1A	11A	21A	31A	41A	51A	No. of stain
	300	250	200	150	100	50	Wt. of whiting
	0.152	0.152	0.152	0.152	0.152	0.152	Wt. of Cr_2O_3
	377.15	349.15	321.15	293.15	265.15	237.15	Comb. Wt.
0.005	2A	12A	22A	32A	42A	32A	No. of stain
	300	250	200	150	100	50	Wt. of whiting
	0.76	0.76	0.76	0.76	0.76	0.76	Wt. of Cr_2O_3
	377.76	349.76	321.76	293.76	261.76	237.76	Comb. Wt.
0.01	3A	13A	23A	33A	43A	53A	No. of stain
	300	250	200	150	100	50	Wt. of whiting
	1.52	1.52	1.52	1.52	1.52	1.52	Wt. of Cr_2O_3
	378.52	350.52	322.52	294.52	266.52	238.52	Comb. Wt.
0.02	4A	14A	24A	34A	44A	54A	No. of stain
	300	250	200	150	100	50	Wt. of whiting
	3.04	3.04	3.04	3.04	3.04	3.04	Wt. of Cr_2O_3
	380.4	352.4	324.4	296.4	268.4	240.4	Comb. Wt.
0.03	5A	15A	25A	35A	45A	55A	No. of stain
	300	250	200	150	100	50	Wt. of whiting
	4.56	4.56	4.56	4.56	4.56	4.56	Wt. of Cr_2O_3
	381.56	353.56	325.6	297.56	269.56	241.56	Comb. Wt.
0.05	6A	16A	26A	36A	46A	56A	No. of stain
	300	250	200	150	100	50	Wt. of whiting
	7.6	7.6	7.6	7.6	7.6	7.6	Wt. of Cr_2O_3
	384.6	356.6	328.6	300.6	272.6	244.6	Comb. Wt.
0.075	7A	17A	27A	37A	47A	57A	No. of stain
	300	250	200	150	100	50	Wt. of whiting
	11.4	11.4	11.4	11.4	11.4	11.4	Wt. of Cr_2O_3
	388.4	360.6	332.2	304.4	276.4	248.4	Comb. Wt.
0.1	8A	18A	28A	38A	48A	58A	No. of stain
	300	250	200	150	100	50	Wt. of whiting
	15.2	15.2	15.2	15.2	15.2	15.2	Wt. of Cr_2O_3
	392.2	364.2	336.2	308.2	280.2	252.2	Comb. Wt.
0.125	9A	19A	29A	39A	49A	59A	No. of stain
	300	250	200	150	100	50	Wt. of whiting
	19	19	19	19	19	19	Wt. of Cr_2O_3
	396.	368	340	312	284	256	Comb. Wt.
0.15	10A	20A	30A	40A	50A	60A	No. of stain
	300	250	200	150	100	50	Wt. of whiting
	22.8	22.8	22.8	22.8	22.8	22.8	Wt. of Cr_2O_3
	399.8	371.8	343.8	315.8	287.8	259.8	Comb. Wt.

CHART II.

Showing Molecular and Batch Formula, and Combining Weight for Stains in *Group B.*

CHROMATE OF LEAD.

Eqv. Cr_2O_3	Eqv. CaO. 3.0	2.50	2.00	1.50	1.00	0.50	
0.001	1B	11B	21B	31B	41B	51B	No. of stain
	300	250	200	150	100	50	Wt. of whiting
	0.646	0.646	0.646	0.646	0.646	0.646	Wt. of $PbCrO_4$
	377.65	349.65	321.65	293.65	265.65	237.65	Comb. Wt.
0.005	2B	12B	22B	32B	42B	52B	No. of stain
	300	250	200	150	100	50	Wt. of whiting
	3.23	3.23	3.23	3.23	3.23	3.23	Wt. of $PbCrO_4$
	380.23	352.23	324.23	296.23	268.23	240.23	Comb. Wt.
0.01	3B	13B	23B	33B	43B	53B	No. of stain
	300	250	200	150	100	50	Wt. of whiting
	6.46	6.46	6.46	6.46	6.46	6.46	Wt. of $PbCrO_4$
	383.46	355.46	327.46	299.46	271.46	243.46	Comb. Wt.
0.02	4B	14B	24B	34B	44B	54B	No. of stain
	300	250	200	150	100	50	Wt. of whiting
	12.92	12.92	12.92	12.92	12.92	12.92	Wt. of $PbCrO_4$
	389.92	361.92	333.92	305.92	277.92	249.92	Comb. Wt.
0.03	5B	15B	25B	35B	45B	55B	No. of stain
	300	250	200	150	100	50	Wt. of whiting
	19.38	19.38	19.38	19.38	19.38	19.38	Wt. of $PbCrO_4$
	396.38	368.38	340.38	312.38	284.38	256.38	Comb. Wt.
0.05	6B	16B	26B	36B	46B	56B	No. of stain
	300	250	200	150	100	50	Wt. of whiting
	32.3	32.3	32.3	32.3	32.3	32.3	Wt. of $PbCrO_4$
	409.3	381.3	353.3	325.3	297.3	269.3	Comb. Wt.
0.075	7B	17B	27B	37B	47B	57B	No. of stain
	300	250	200	150	100	50	Wt. of whiting
	48.45	48.45	48.45	48.45	48.45	48.45	Wt. of $PbCrO_4$
	425.45	397.45	369.45	341.45	313.45	285.45	Comb. Wt.
0.1	8B	18B	28B	38B	48B	58B	No. of stain
	300	250	200	150	100	50	Wt. of whiting
	64.6	64.6	64.6	64.6	64.6	64.6	Wt. of $PbCrO_4$
	441.6	413.6	385.6	357.6	329.6	301.6	Comb. Wt.
0.125	9B	19B	29B	39B	49B	59B	No. of stain
	300	250	200	150	100	50	Wt. of whiting
	80.75	80.75	80.75	80.75	80.75	80.75	Wt. of $PbCrO_4$
	457.75	429.75	401.75	373.75	345.75	317.75	Comb. Wt.
0.15	10B	20B	30B	40B	50B	60B	No. of stain
	300	250	200	150	100	50	Wt. of whiting
	96.9	96.9	96.9	96.9	96.9	96.9	Wt. of $PbCrO_4$
	473.9	445.9	417.9	389.9	361.9	333.9	Comb. Wt.

CHART III.

Showing Molecular and Batch Formulae, and Combining Weight for Stains in *Group C.*

POTASSIUM DICHROMATE.

Eqv. Cr_2O_3	Eqv. CaO. 3.0	2.50	2.00	1.50	1.00	0.50	
0.001	1C	11C	21C	31C	41C	51C	No. of stain
	300	250	200	150	100	50	Wt. of whiting
	.294	.294	.294	.294	.294	.294	Wt. of $K_2Cr_2O_7$
	377.2	348.5	321.9	293.3	265.3	237.3	Comb. Wt
0.005	2C	12C	22C	32C	42C	52C	No. of stain
	300	250	200	150	100	50	Wt. of whiting
	1.47	1.47	1.47	1.47	1.47	1.47	Wt. of $K_2Cr_2O_7$
	378.5	350.5	322.6	294.5	266.5	238.3	Comb. Wt.
0.01	3C	13C	23C	33C	43C	53C	No. of stain
	300	250	200	150	100	50	Wt. of whiting
	2.94	2.94	2.94	2.94	2.94	2.94	Wt. of $K_2Cr_2O_7$
	379.9	351.9	323.9	295.9	267.9	234.9	Comb. Wt.
0.02	4C	14C	24C	34C	44C	54C	No. of stain
	300	250	200	150	100	50	Wt. of whiting
	5.88	5.88	5.88	5.88	5.88	5.88	Wt. of $K_2Cr_2O_7$
	382.9	354.9	326.9	298.9	270.9	242.9	Comb. Wt.
0.03	5C	15C	25C	35C	45C	55C	No. of stain
	300	250	200	150	100	50	Wt. of whiting
	8.82	8.82	8.82	8.82	8.82	8.82	Wt. of $K_2Cr_2O_7$
	385.8	357.8	329.8	301.8	273.8	245.8	Comb. Wt.
0.05	6C	16C	26C	36C	46C	56C	No. of stain
	300	250	200	150	100	50	Wt. of whiting
	12.7	12.7	12.7	12.7	12.7	12.7	Wt. of $K_2Cr_2O_7$
	389.7	361.7	333.7	305.7	277.7	249.7	Comb. Wt.
0.075	7C	17C	27C	37C	47C	57C	No. of stain
	300	250	200	150	100	50	Wt. of whiting
	22.05	22.05	22.05	22.05	22.05	22.05	Wt. of $K_2Cr_2O_7$
	399.1	371.1	343.1	315.1	287.1	259.1	Comb. Wt.
0.1	8C	18C	28C	38C	48C	58C	No. of stain
	300	250	200	150	100	50	Wt. of whiting
	29.4	29.4	29.4	29.4	29.4	29.4	Wt. of $K_2Cr_2O_7$
	406.4	378.4	350.4	322.4	294.4	266.4	Comb. Wt.
0.125	9C	19C	29C	39C	49C	59C	No. of stain
	300	250	200	150	100	50	Wt. of whiting
	36.75	36.75	36.75	36.75	36.75	36.75	Wt. of $K_2Cr_2O_7$
	413.8	385.8	357.8	339.8	301.8	273.8	Comb. Wt.
0.15	10C	20C	30C	40C	50C	60C	No. of stain
	300	250	200	150	100	50	Wt. of whiting
	44.1	44.1	44.1	44.1	44.1	44.1	Wt. of $K_2Cr_2O_7$
	426.1	393.1	365.1	347.1	309.1	281.1	Comb. Wt.

PREPARATION OF STAIN.

Weighing: Each stain was weighed separately. Cross blending, before or after calcination, was considered impractical and undesirable.

Mixing: All materials were fine enough to pass a 100-mesh sieve, hence, each stain was first passed through a 60-mesh sieve several times and then thoroughly mixed with a spatula.

Calcining: About 125 grams of each stain was calcined in fire clay crucibles of about 4 inches in depth. Each group of 60 stains was calcined separately in a Caulkins gas muffle to cone 5, down. The time consumed in each case was thirteen hours, the stains being allowed to soak two hours after the desired temperature had been reached. By this heat treatment, a fairly uniform distribution was secured and factory conditions closely approximated.

THE GLAZE.

Molecular Formula: The glaze used (inclusive of stain) has the molecular composition shown below. This glaze was chosen because with it was obtained the best sample of chromium-tin red color known to the writers.

$$\left.\begin{matrix} *0.22\ PbO \\ 0.60\ CaO \\ 0.18\ KNaO \end{matrix}\right\} \quad \left.\begin{matrix} 0.16\ Al_2O_3 \\ 0.1\ SnO_2 \\ x\ Cr_2O_3 \end{matrix}\right\} \quad \left\{\begin{matrix} 2.1\ SiO_2 \\ 0.475\ B_2O_3 \end{matrix}\right.$$

All glazes made in the study here reported have this general formula. The only variations in the molecular formula of the several glazes are:

(1) That of the Cr_2O_3 equivalents.

(2) The negligible** amount of PbO and K_2O introduced respectively by the lead chromate and the potassium dichromate.

This uniformity in the molecular composition of the several glazes was designed to throw all of the variations into the stains.

*The molecular formula is inclusive of the stain.
**Arbitrarily so considered in these experiments.

The Fritt: In deciding what portion of this glaze to fritt, the following considerations were made:

(1) The highest calcium content of any of the stains was 3.0 equivalents. Since 0.1 equivalent of the stain was used in each case, the maximum equivalent of CaO introduced by the stain would be 0.3 equivalents. This leaves 0.3 to be added by either the fritt or as calcium carbonate. In all cases, aside from those in which stains having the maximum calcium are used, there will of necessity be an addition of raw calcium, no matter what equivalent of calcium is used in the fritt, hence the maximum possible, or 0.3 equivalents CaO, was made a portion of the fritt.

(2) All of the 0.18 equivalent KNaO was arbitrarily made a portion of the fritt. This was done to increase the fusibility and decrease the solubility of the fritt.*

(3) All of the Al_2O_3, save 0.05 equivalents, was fritted. This left .05 equivalents of Al_2O_3 to be added as raw clay.

(4) All of the B_2O_3 in the glaze was fritted.

(5) Sufficient SiO_2 was added to the fritt to make the oxygen ratio of the fritt the same as that of the glaze. This resulted in the fritting of 0.11 equivalents of SiO_2. This arbitrary rule based on the equality of the oxygen ratios was suggested by Purdy and Fox in their fritted glaze treatise.** It results in the fritting of approximately 50% of the glaze which is by many used as a basis on which to determine how much of the glaze to fritt.

Assembling, we have as the portion selected for fritting:

0.30	CaO	0.11 Al_2O_3	0.826 SiO_2
0.18	KNaO		0.475 B_2O_3
0.48			

*A thin crust appeared on top of the ground fritt when dried in pans after grinding. None of the water used in the grinding was removed prior to drying, hence, this thin crust was largely the soluble portion of the fritt, together with the very finest particles of the insoluble portion.

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When reduced to RO unity, this fritt is

0.625 CaO	0.23 Al_2O_3	.72	SiO_2
0.375 KNaO		0.989	B_2O_3
1.000			

259.475 equals combining weight.

All glazes, therefore, contain 0.48 equivalents of fritt. The batch formula of this fritt is

30.0 Whiting.
38.2 Borax.
34.1 Boracic Acid (flaky).
44.48 Feldspar (Brandywine).
7.78 Kaolin (American).
17.16 Flint (Golding).

The fritt batch was thoroughly mixed by sieving. It was then melted in a large crucible which permitted a continuous operation, the fused portion dropping into and being granulated by cold water. Three hours in a gas furnace was sufficient to melt this fritt. The fritt was next ground five hours in porcelain ball mills, passed through a 150-mesh sieve without residue and dried in enameled iron pans.

Batch Formula of Glaze. The batch formula of the glaze was

0.48 equivalent fritt	124.55	
0.22 equivalent carbonate of lead	56.76	
1.074 equivalent flint	64.44	
0.05 equivalent clay	12.90	
		258.65

0.1 equivalent stain
y equivalent whiting

The quantities of fritt, carbonate of lead, flint and clay common to all the glazes, were weighed, ground three hours in a ball mill and passed without residue through a 150-mesh screen. This batch constituted the "glaze stock" to which the 0.1 equivalent of stain and the required whiting were added. Thirty grams of this "glaze stock" were used for each glaze.

Application of Glaze to the Body. Biscuit tile 3 inch x 1½ inch were used. They were first saturated in distilled water.*

*To prevent flaking off of the glaze upon drying.

Each glaze was mixed thoroughly and worked up to a thick paste with distilled water by means of a spatula on a ground glass plate. Four tile were coated to a thickness of about 1/16 inch with each glaze.

BURNING OF GLAZED TILE.

The tile were placed on setters carefully luted and burned in a down-draft muffle kiln. Three burns in all were made as here noted.

Burn 1. The heat was raised gradually to cone 01 in 29 hours. The fires were drawn and dampers left open. A uniform distribution of heat was obtained. Coke was used exclusively.

Burn 2. A dark red was reached at the end of 12 hours and the temperature gradually raised until cone 01 was reached after 27 hours firing. Cone 2 was touching at the end of 30 hours. The fires were drawn and the damper left open to allow rapid cooling. Cone 2 was down in all parts of the muffle. Coke was used, supplemented with soft coal occasionally.

Burn 3. Both coke and coal (2:1) were used. The coal was first coked on the coking plate in the front of the grate bars. The firing was at intervals of about 20 minutes, the temperature being raised gradually. At the end of 23 hours cone 06 was down and after 27 hours cone 1 was flat. Cone 3 was down at the end of 31 hours. The burn was uniform. The fire was drawn, dampers opened, and the kiln allowed to cool rapidly.

RESULTS

THE STAINS.

Group A. In this group are those stains in which the chromium was added as Cr_2O_3. The stains of this group came from the crucibles in the form of friable cakes, easily broken up with a spatula. In all of these stains small white specks were visible to the naked eye.

COLOR CHART — GROUP "A" STAINS.

$CaCO_3$	Cr_2O_3 .001	.005	.010	.020	.030	.050	.075	.100	.125	.150
3.00	1A ← Light	2A Yellow →	3A ←	4A	5A Light	6A Green	7A to	8A Brown	9A	10A →
2.50	11A ←	12A Light Yellow	13A →	14A ←	15A Light	16A to	17A Dark	18A Brown	19A	20A →
2.00	21A ←	22A	23A	24A Light	25A Pink	26A to	27A Dark	28A Pink	29A	30A →
1.50	31A ←	32A	33A	34A Light	35A Pink	36A to	37A Dark	38A Pink	39A	40A →
1.00	41A ←	42A	43A	44A Light	45A Pink	46A to	47A Dark	48A Pink	49A	50A →
0.50	51A ←	52A	53A	54A Light	55A Pink	56A to	57A Dark	58A Green	59A	60A →

Samples of each were preserved in small bottles for color comparison.

The accompanying chart gives the range of colors shown by these stains.

It will be noted that in the high-lime series (3.0 equivalent) no pink color was developed. In the stains containing 2.5 equivalents of lime, the stains with high chromium have a brownish tint. The stains containing 2.00, 1.50 and 1 equivalents of lime developed more pinks, the pink tint increasing in intensity with increase of chromium.

In the series containing 0.5 equivalents of lime, the green tint re-occurs. The accompanying chart shows the range of colors for Group A Stains.

Group B. In this group are those stains in which the chromium was added as $PbCrO_4$. The stains from this group came from the crucibles in soft cakes. Small white specks were visible in all of the stains.

Samples of each were preserved for color comparison.

The accompanying chart shows the range of colors of the Group B stains. It will be noted that the stains of this group differ from the stains of Group A, in that the developed tints are erratic in their occurrence. For instance, in the stains containing 3.0 equivalents of lime, stains No. 6, No. 7, and No. 8 have a marked pink color, while stains No. 5, No. 9 and No. 10 are greenish. In the series containing 2.5 equivalents of lime, stains No. 16 and No. 17 showed a marked pink color. In the stains containing 2.00, 1.50, 1.00 and 0.50 equivalents of lime, the color ranged from white to pink, the pink color gradually increasing with the increase of $PbCrO_4$.

Group C. The stains in this group are those in which the chromium is derived from $K_2Cr_2O_7$. The stains of this group came from the crucibles in soft friable masses. When placing the crucibles in the kiln, some stain was accidentally dropped on the kiln bottom. It was found on drawing that the crucible placed over this spilled stain

COLOR CHART — GROUP "B," STAINS.

	PbO. 002	PbO .010	PbO .020	PbO .040	PbO .060	PbO .100	PbO .150	PbO .200	PbO .250	PbO .300
	Cr_2O_3 .001	Cr_2O_3 .005	Cr_2O_3 .010	Cr_2O_3 .020	Cr_2O_3 .030	Cr_2O_3 .050	Cr_2O_3 .075	Cr_2O_3 .100	Cr_2O_3 .125	Cr_2O_3 .150
3.00	1B ←	2B Light	3B Yellow	4B →	5B ←	6B Pink	7B	8B →	9B Light	10B Green →
2.50	11B ←	12B Light	13B Yellow	14B →	15B ←	16B Pink	17B →	18B ←	19B Light	20B Gray →
2.00	21B ←	22B	23B	24B Light	25B Pink	26B to	27B Pink	28B	29B	30B →
1.50	31B ←	32B	33B	34B Light	35B Pink	36B to	37B Pink	38B	39B	40B →
1.00	41B ←	42B	43B	44B White	45B to	46B Light	47B Pink	48B	49B	50B →
0.50	51B ←	52B	53B	54B White	55B to	56B Light	57B Pink	58B	59B	60B →

had a mass of green crystals incrusted on its bottom, probably due to the volatilization of chromium.

It was also noted that in the case of stains containing 0.05 or more equivalents of $K_2Cr_2O_7$, green crystals had formed near the tops of the crucibles. This did not occur in any case in either the A or the B Group, the crucibles being perfectly clean after the stains were removed. The cones (*) used in the burn of Group C had a light green color and masses of green crystals were imbedded upon them.

Samples of the stains of this series were placed in bottles and preserved for color comparison.

Following is a chart showing the color range secured.

The stains having 3.00 equivalents of $CaCO_3$ ranged from a light green to a rich brown with high chromium. The stains with 2.5 equivalents of $CaCo_3$ ranged from light to dark browns. With 2.00, 1.50 and 1.00 equivalents of $CaCO_3$, the predominating colors were pink, while with .50 equivalents of $CaCO_3$ the color ranged from lilac to light green.

Comparison of Colors Secured in the Stains of Groups A, B and C. In Group A (oxide of chromium) occurred the largest number of stains having a pink color, similar to the color of those found on the market.

In Group B (lead chromate) the pinks were very much lighter than those found in either Group A or Group C. In Group C (potassium dichromate) there was, in addition to the characteristic pinks, dark brown colors in those stains which were high in chromium.

It was also noted in this group that when water was added to the stains containing high chromium, after standing a few minutes, the pink color was lost and the stains assumed a light yellowish-brown color, probably due to the bringing to the surface of brown chromic acid. The stains that developed this brown color most were those containing from 0.050 to 0.15 equivalents of chromium.

*See Burt, Volume VI, page 153, *Am. Ceramic Soc. Trans.*

COLOR CHART — GROUP "C," STAINS.

	K_2O .001	K_2O .005	K_2O .010	K_2O .020	K_2O .030	K_2O .050	K_2O .075	K_2O .100	K_2O .125	K_2O .150
	Cr_2O_3 .001	Cr_2O_3 .005	Cr_2O_3 .010	Cr_2O_3 .020	Cr_2O_3 .030	Cr_2O_3 .050	Cr_2O_3 .075	Cr_2O_3 .100	Cr_2O_3 .125	Cr_2O_3 .150
3.00	1C ←	2C	3C Light	4C Green	5C →	← 6C	7C	8C Brown	9C	10C →
2.50	11C ←	12C	13C	14C Light	15C Brown	16C to	17C Dark	18C Brown	19C	20C →
2.00	21C ←	22C	23C	24C Light	25C Pink	26C to	27C Dark	28C Brown	29C	30C →
1.50	31C ←	32C	33C	34C Light	35C Pink	36C to	37C Dark	38C Pink	39C	40C →
1.00	41C ←	42C	43C	44C Light	45C Pink	46C to	47C Brown	48C	49C	50C →
0.50	51C ←	52C	53C	54C Lilacs	55C to	56C Light	57C Green	58C	59C	60C →

As will be shown later, the color of the stain is not a criterion of what the tint (developed in the glaze) will be.

THE GLAZES.*

Group A.

Cone 01 *Burn.* There was no crazing, crawling or shivering exhibited on any of the tile and all appeared to have been equally matured. This would tend to show that the difference in composition of the stains added did not materially affect the refractory quality of the glaze. It was thought, however, that all of the trials were slightly immature and hence the burns at higher cones. The colors secured with the Group A stains are shown on the accompanying chart.

It was noted that in all of the glazes of this group burned to cone 01, a milky segregation was in evidence. This segregation is similar to that which is produced when tin oxide is used raw. The effect was quite pleasing in most cases.

Cone 1—2 *Burn.* The effect of this higher heat treatment brought the glaze to complete maturity, but did not materially affect or alter the colors obtained at cone 01.

It was also noted that the milky segregation though still noticeable, was not in evidence to such a large extent and in some cases had disappeared completely.

Cone 3 *Burn.* The glazes of this series were well matured. The colors were, in most cases, slightly inferior to those secured on the tile burned at the lower temperature, i. e., they were faded somewhat. The milky segregations noted in the cone 01 burn, was evident in a larger degree than in either of the other two burns.

Group B.

Cone 01 *Burn.* The condition the glazes was fairly good, all very closely approximating maturity.

*The same system of numbering used in the stains was continued with the glazes. For instance, the glaze in which stain 9A was used was marked 9A, etc.

COLOR CHART — GROUP "A," GLAZES.

$CaCO_3$	Cr_2O_3 .001	.005	.010	.020	.030	.050	.075	.100	.125	.150
3.00	1A ←	2A Pinks	3A →	4A ←	5A	6A Browns	7A →	8A ← and Mottled	9A Greens Browns	10A →
2.50	11A ←	12A Pinks	13A →	14A ←	15A Reddish Browns	16A →	17A ←	18A Greens	19A	20A →
2.00	21A ←	22A	23A Lilacs	24A	25A →	26A ←	27A Sage	28A Green	29A	30A →
1.00	31A ←	32A	33A Lilacs	34A →	35A ←	36A	37A Sage	38A Green	39A	40A →
1.50	41A ←	42A	43A Lilacs	44A →	45A ←	46A Reddish	47A Green	48A to	49A Green	50A →
0.50	51A ←	52A	53A Lilacs	54A →	55A ←	56A Light	57A to	58A Dark	59A Green	60A →

COLOR CHART — GROUP "B," GLAZES.

	PbO. 002	PbO .010	PbO .020	PbO .040	PbO .060	PbO .100	PbO .150	PbO .200	PbO .250	PbO .250
	Cr_2O_3 .001	Cr_2O_3 .005	Cr_2O_3 .010	Cr_2O_3 .020	Cr_2O_3 .030	Cr_2O_3 .050	Cr_2O_3 .075	Cr_2O_3 .100	Cr_2O_3 .125	Cr_2O_3 .150
3.00	1B ←	2B	3B Pinks	4B	5B →	6B ←	7B Good	8B Reds	9B	10B →
2.50	11B ←	12B	13B Pinks	14B	15B →	16B ←	17B Good	18B Reds	19B	20B →
2.00	21B ←	22B Lilacs	23B	24B →	25B ←	26B Reds	27B	28B →	29B ← Mottled	30B Reds →
1.50	31B ←	32B	33B Lilacs	34B	35B →	36B ←	37B Opaque	38B Reds	39B	40B →
1.00	41B ←	42B	43B	44B Lilacs	45B	46B	47B	48B	49B	50B →
0.50	51B ←	52B	53B	54B Lilacs	55B	56B	57B →	58B ←	59B Opaque Lilacs	60B →

COLOR CHART — GROUP "C," GLAZES.

	K_2O .001	K_2O .005	K_2O .010	K_2O .020	K_2O .030	K_2O .050	K_2O .075	K_2O .100	K_2O .125	K_2O .150
	Cr_2O_3 .001	Cr_2O_3 .005	Cr_2O_3 .010	Cr_2O_3 .020	Cr_2O_3 .030	Cr_2O_3 .050	Cr_2O_3 .075	Cr_2O_3 .100	Cr_2O_3 .125	Cr_2O_3 .150
3.00	1C ←	2C Pink to Red	3C →	4C ←	5C Dark Browns	6C →	7C ←	8C Mottled Greens	9C and Browns	10C →
2.50	11C ←	12C Pink	13C →	14C ←	15C Dark Brown	16C →	17C ←	18C Mottled Greens	19C and Browns	20C →
2.00	21C ← Pink	22C →	23C ←	24C Reds	25C →	26C ←	27C Browns	28C →	29C ← Browns and Greens	30C →
1.50	31C ← Pink	32C →	33C ←	34C Reds	35C →	36C ←	37C Mottled	38C Browns	39C and Greens	40C →
1.00	41C ← Pink	42C →	43C ←	44C Dark	45C Red	46C to	47C Dark	48C Brown	49C	50C →
0.50	51C ←	52C Good Pinks	53C →	54C ←	55C Dark Reds	56C →	57C	58C Mottled Reds	59C and Browns	60C →

The colors developed are shown in the accompanying chart.

The milky segregation spoken of in Group A was in evidence on all of the trials of this group.

Cone 1—2 *Burn.* The higher heat treatment improved the glaze. Although there was but a slight difference in tint, the colors were better and the milky segregation was much less in evidence.

Cone 3 *Burn.* The colors were about the same as in the other two burns. The milky segregation had again increased and was greater than that observed in either Burn No. 1 or Burn No. 2.

Group C.

Cone 01 *Burn.* The glazes were all fairly well developed.

The accompanying chart shows the colors secured.

The milky segregation was in evidence to a less marked degree than in the other two groups.

Cone 1—2 *Burn.* The higher heat treatment seemed to have improved both the color and condition of the glaze.

The milky segregation was entirely absent in a majority of the trials.

Cone 3 *Burn.* The higher temperature seems to again have been slightly detrimental to the colors obtained. The milky segregation was more in evidence than in previous burns.

COLORS OBTAINED.

In the foregoing charts are given the general trend in development of the colors. These charts, however, could not be made sufficiently specific to convey a proper idea of the exact shades. For this reason the following more-detailed statements are made.

Before making these statements, attention is again called to the fact that none of these stains were washed, or recalcined; that many showed very strongly the soluble

chromic acid which came to the surface before and especially after the glazed tiles had dried. That this surface-film of soluble chromic acid has affected very materially the resultant tints seems to the writers to be logical reasoning. The descriptions here given, therefore, are only of the results actually obtained and not of what might have been obtained had the stains been washed and recalcined.*

In the following, the glazes are grouped according to color.

Fine Reds.

16 — 20 B inclusive, cone 01 — 2.
25 — 28 B inclusive, cone 01 — 2.
11 — 12 C inclusive, cone 2.

Possible Fine Reds.

11 — 13 A inclusive, cone 01 — 2.
21 — 23 A inclusive, cone 01 — 2.
31 A inclusive, cone 01 — 2.
1 — 8 B inclusive, cone 01 — 3.
1 — 2 C inclusive, cone 01 — 3.
21 — 23 C inclusive, cone 01 — 3.
31 — 33 C inclusive, cone 01 — 3.
41 — 43 C inclusive, cone 01 — 3.
51 — 53 C inclusive, cone 01 — 3.

Brownish Reds. (Similar to Seger's).

3 — 4 C inclusive, cone 01 — 2.
13 — 15 C inclusive, cone 01 — 2.
24 — 26 C inclusive, cone 01 — 3.
34 — 36 C inclusive, cone 01 — 3.
44 — 46 C inclusive, cone 01 — 3.
54 — 56 C inclusive, cone 01 — 3.

*Washing and recalcining of the stains was reserved for further work. It was thought important that results should be obtained before and after washing and recalcining, that definite statements may be made in regard to this extra step in the preparation of the stains.

Pink and Light Reds.

11 — 12 A inclusive, cone 01 — 3.
21 — 22 A inclusive, cone 01 — 3.
1 — 5 B inclusive, cone 01 — 3.
11 — 15 B inclusive, cone 01 — 3.
21 — 24 B inclusive, cone 01 — 3.
1 — 2 C inclusive, cone 01 — 3.
11 — 12 C inclusive, cone 01 — 3.
21 — 22 C inclusive, cone 01 — 3.
31 — 32 C inclusive, cone 01 — 3.

Lilac.

21 — 23 A inclusive, cone 3.
31 — 33 A inclusive, cone 2 — 3.
41 — 43 A inclusive, cone 01 — 3.
51 — 53 A inclusive, cone 01 — 3.
21 — 24 B inclusive, cone 3.
31 — 33 B inclusive, cone 2 — 3.
34 — 36 B inclusive, cone 3.
41 — 47 B inclusive, cone 2 — 3.
51 — 56 B inclusive, cone 01 — 3.

Cool Purple Grey. ("Elephant's Breath").

57 — 60 B inclusive, cone 01 — 3.
49 — 50 B inclusive, cone 2 — 3.

Seal Browns.

5 — 7 A inclusive, cone 01 — 3.
5 — 8 C inclusive, cone 1 — 2.
17 — 19 C inclusive, cone 1 — 3.
26 — 30 C inclusive, cone 01 — 2.
37 — 40 C inclusive, cone 01 — 2.
45 — 50 C inclusive, cone 01 — 3.
56 — 60 C inclusive, cone 01 — 2.

Greens.

8 — 10 A inclusive, cone 01 — 3, mottled, poor.
9 — 10 C inclusive, cone 01 — 3, mottled, good.
8 C, cone 3.
20 C, cone 01 — 3.

Greens (Cont'd).

19 C cone 3.
29 — 30 C inclusive, cone 3.
40 C cone 3.
60 C cone 3.

Sage Greens.

17 — 20 A inclusive, cone 1 — 2, shading into turquoise at 3.
26 — 30 A inclusive, cone 1 — 3.
36 — 40 A inclusive, cone 1 — 3.
46 — 50 A inclusive, cone 1 — 3.
56 — 60 A inclusive, cone 01 — 3.

CONCLUSIONS.

Variation due to difference in source of chromium. Rodgers and Mellor* used as sources of chromium for chromium-tin pink stains, chromic acid, potassium dichromate potassium chromate, potassium tetrachromate, tin chromate, calcium chromate, and chromic oxide. They conclude that the tint obtained is practically independent of the source of chromium.

Seger** says, "Outside of the potassium chromate, quite a number of substances produce the same effect, but it is safest to work with potassium chromate."

Purdy* says in regard to the use of chromic acid by Hull, "Its end reaction on the other ingredients cannot be the same as that of the other chrome compounds."

Hull** in reply to Purdy, asks, "Is the use of an unusual agent to prove a point in research an objectionable feature of the research?" Must we confine ourselves to those substances already in common use? . . . However, if one ingredient helps to produce one so-called end reaction and a second compound produces something of which the

*English Ceramic Society 1905, p. 66, "Effect of Chromium Obtained from Different Sources."
**Quoted by Hull, American Ceramic Society, Vol. IV, p. 231.
*American Ceramic Society, Vol. V, p. 250.
**American Ceramic Society, Vol. VI, p. 152.

color is as good as the first, why should we not use the latter if convenient? . . . Seger's formulae had already shown that lead was not required, so why use lead chromate?

In the above quotations, Rodgers and Mellor, Seger, and Hull, either state or infer that it makes no difference what source of chromium is used. Purdy says that it does.

Rodgers and Mellor's stain reduced to a molecular formula is (approximately):

$$\left.\begin{matrix} 0.83\ CaO \\ 0.05\ PbO \\ 0.03\ Na_2O \end{matrix}\right\} \quad \left.\begin{matrix} 1.0\ SnO_2 \\ 0.046\ Cr_2O_3 \end{matrix}\right\} \quad \left\{\begin{matrix} 1.0\ SiO_2 \\ 0.08\ B_2O_3 \end{matrix}\right.$$

This stain is, compared to those used in the present study, between Nos. 45 and 46, so far as the Cr_2O_3 content is concerned, and between these and Nos. 55 and 56 in regard to the CaO content. These four sets of stains *were* nearly alike in resultant tint (in the glaze) with chromium oxide and lead chromate. With potassium dichromate, however, a very decidedly *different result* was obtained. With chromium oxide and lead chromate these four stains gave pale lilac tints, while with potassium dichromate they gave very dark brownish reds.

The discrepancy between the results obtained by Rodgers and Mellor and those here reported may be due to (1) error, (2) difference of firing conditions, or (3) the fact that the stains here reported were not washed and recalcined. That this discrepancy is due to an error is hardly likely. In the present case each of the stains was weighed, mixed and calcined separately and added to portions of the same glaze stock. This discrepancy may be due to difference in firing conditions. In the present case, however, all glazes of the three groups were burned together, three different times, and at a different finishing heat each time and yet, so far as the glazes containing stains 45, 46, 55 and 56 are concerned, the results are constant, i. e., no differences are noticeable beyond those induced by difference in the source of the chromium. If the

discrepancy between Rodgers' and Mellor's and the present results is due to want of washing and recalcining in the latter, it will be demonstrated when that phase of the subject has been worked out. It would hardly seem possible, however, that mere washing and recalcining would convert lilacs into reds or reds into lilacs.

A further discrepancy is to be noted in that with chromium oxide and lead chromate, the colors (in the glaze) obtained with the stains most nearly like those of Rodgers and Mellor are decidedly lilac, with no trace of a pink tint. This may be due to differences in the glazes used, but it is hardly likely that this is possible.*

Apropos to Seger's statement of the effect of various sources of chromium, it must be granted that Hull's results with chromic acid and the present results with potassium dichromate, in those stains** which are most nearly like Seger's in composition, check the usual experience in that they give brownish reds that disseminate with difficulty. With chromium oxide and lead chromate, however, the resulting color is lavender. This is contradictory to Seger's observation in regard to the constancy of tint irrespective of the source of chromium.

Reference to the list of stains which produce like color effects is sufficient to prove that Seger's observation can not have a broad application. Very rarely do stains of the same molecular composition*** but with different sources of chromium give the same color effect. At the present stage of these investigations it appears to be a case of an exception, rather than a rule, for stains of like molecular composition, but different chromium source to coincide in their resultant color production.

(2) The only means Hull used in studying his results was color comparison. On this basis, the experiments here

*Rodgers and Mellor do not give the formula of the glaze they used. It is inferred that they used their stains as under-glaze colors while in the present case the stains were used in the glazes.

**No. 45 and 55.

***Disregarding the K_2O and PbO introduced by the $K_2Cr_2O_7$ and $PbCrO_4$.

(2) The title of Hull's treatise was "The Constitution of Chromium-Tin Pink." His research was, however, like the present one, an empirical study of the effect of variation in composition of the stain on the color producable in a glaze. He made no attempt to study the constitution of his stains.

reported prove most emphatically that he is in error when he affirms that the employment of an unusual source of chromium in a research (as he conducted his and the present one has been conducted and is now being considered) an objectionable feature of that research *when that unusual source is the only source.*

The "end reactions" for colors produced in the present investigation *were different, with different chrome compounds.* To what extent this difference in results can be eliminated by washing and recalcining of the stains remains to be seen.

It is wholly impartial to state that the research here reported emphasizes what Purdy stated had been his factory experience, namely, that different color results are obtained with different chrome compounds.

Limits of Variation in Equivalents of Cr_2O_3: According to Rix*, "It appears that only the merest trace of chromium oxide is necessary to the development of the pink." This observation has been made by others and is confirmed in these studies. 0.0001 equivalent Cr_2O_3 with high calcium produced light reds in each of the three groups. With decrease in calcium, the tint produced by 0.0001 equivalent of Cr_2O_3 changed to lilac in Group A and B, but apparently increased from light to a very good red in Group C.

Hull asserts** that his "Series A-1 indicates that the quantity of chromic oxide (0.0375 equiv.) *** is as high as is allowable." With chromium oxide and potassium dichromate as sources of chromium, the present investigation checks Hull's observation. With lead chromate as a source, however, the "allowable" limit was not reached, for 0.15*** equivalent gave good reds, except when the CaO was reduced to 1.0*** equivalent. In these latter cases the resulting color was more of a lilac.

*English Ceramic Society.

**American Ceramic Society *Transactions*, Vol. IV, p. 236.

***Equivalents in the stain. Only 0.1 equivalent of these were introduced into the glaze.

Effect of Variation of Calcium on Color in the Glaze: From Hull's conclusion it is inferred that the effect on the fusibility of the glaze is the only limiting factor in the amount of calcium that can be used in the stain. The results of the present investigation show that the stain can carry at least 3.0 equivalents of calcium.

Rodgers and Mellor* state that "The color will bear a higher temperature, the greater the proportion of lime up to at least 25%." Results in Group A (Cr_2O_3) and Group B ($PbCrO_4$) check this observation. In Group C ($K_2Cr_2O_7$), however, there was very little difference in tint with variation in heat treatment even with as low as 0.5 equivalent of CaO.

Heath and Rigby found** "Passing from a color composition which contained 25% whiting gradually down through a series of eight experiments to the vanishing point, the tones of color pass from a good pink through varying poor pinks and browns to greyish-brown."

This observation is confirmed by the present work, especially in the lead chromate series. In this series the high lime end gave strong reds but with decrease of lime there was a gradual fading until with 0.5 equivalents of lime a cool purple grey color is produced.

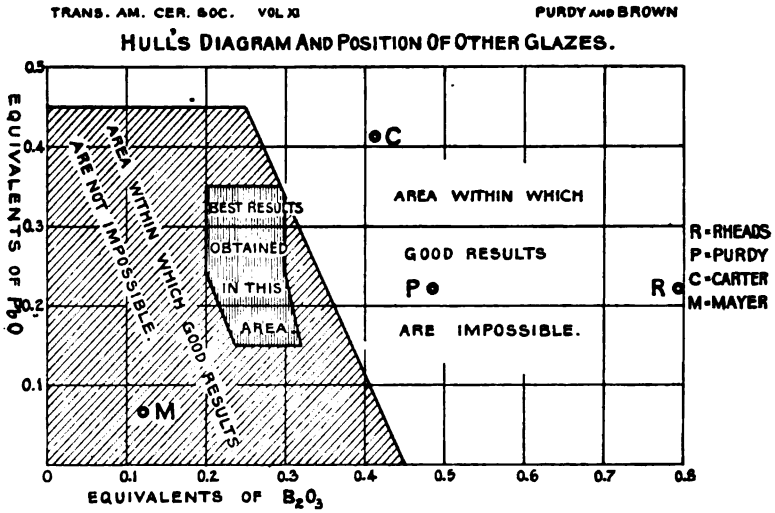
Effect of Variation in Composition of stain on the Refractoriness of the Glaze: No discernible difference was noted in maturity of the glaze due to difference in composition of the stains.

Relative Importance of Stain and Glaze Composition: Much stress has been laid upon the idea that the composition of the glaze is more important than the composition of the chromium-tin pink stain. Quite the reverse of this would, in light of the present investigation, seem to be true. It must be granted that the glaze must be relatively low in lead and alkalies and high in calcium. Beyond these limitations, however, there seems to be very little, if any, that is requisite. That the limits of possible varia-

*Loc. cit.

**English Ceramic Society 1901, p. 5.

tion is more extended than Hull's curves* would lead one to believe can be seen from the curves in Fig. 1.



In Fig. 1, Hull's curves are reproduced in their entirety and in addition the position of other glazes noted. Surely the limits of variation in glaze composition are wider than many suppose.

POSSIBLE REASON FOR NOT CHECKING OBSERVATIONS MADE BY OTHERS.

The large difference in results obtained in the several stains may be due to the following factors:

(1) *Constitution of Lead Chromate Used:* It is a practical observation that lead chromate manufactured by different color makers produces such a difference in tint that this has been used as a means of making a pink and a red, both from the same stain and glaze formula.

(2) *Volatilization of the Potassium Dichromate:* The stains were calcined by a heat treatment that approximated factory conditions (12 hrs. to cone 5). The crucibles were not covered, however, hence volitilization, where there was any, could proceed unhindered.

*P. 251 Ibid.

(3) *Purity of the Chromium Oxide:* The chromium oxide was purchased on the market. There is no record of either where the particular oxide used in these investigations was obtained, or of its purity. It is a well recognized fact, however, that with chromic oxide it takes but a little difference in purity to make a vast difference in the results.

(4) *Solubility of the Stains:* No difference was made in the treatment between the wholly insoluble and partially insoluble stains. As a consequence of this, some of the tiles had a coating of chromic acid come to the surface and others did not.

Since it is uncertain how effective these possible irregularities were, no allowance can be made because of them.

SUGGESTIONS FOR FUTURE WORK.

1. Washing and recalcination. The first five of each of the calcium series, containing .001 to .030 equivalents of chromium should be washed and recalcined.

2. The suggestion by Rodgers and Mellor* "that after the addition of zinc chromate there is less tendency to milky or dull surface, and there is greater range in temperature of firing" offers a remedy for the milky segregation defect.** Zinc chromate should be substituted in part as a source of chromium in the stain, and the stain incorporated into the glaze both with and without washing and recalcination.

3. Addition of chromium to the glaze aside from that introduced by the stain.

4. Determination of amount and character of soluble material obtained after the first calcination of the stain.

5. Use of PbO in stain with chromic oxide.

6. Burning of stains under reducing conditions.

7. Rapid versus slow cooling of the glazes.

*English Ceramic Society, p. 67.

**If it should be considered as a defect.

8. Variation in character of the alkaline earth constituent of the stain and glaze. Bismuth is said to be very favorable to chromium-tin pink tints.

9. Use of more complex stain batches. With the same molecular formula vastly different effects have been produced by merely making variations in the character of materials used.

Stain No. 1 in Table I, page 3, gave a deep blood red in the glaze used in these experiments. In ratio of CaO to Cr_2O_3 it lies between stains 34 and 44, and, on account of the source of Cr_2O_3, would come in Group A. Nos. 34 and 44A, however, were far from being reds.

This blood red commercial stain has as a batch constitution oxide of tin, whiting, flint, soda ash, calcium sulphate and oxide of chromium. On basis of SnO_2 unity, it contains 0.22 equivalent of Na_2O and less than 0.5 equivalent of SiO_2.

It follows, therefore, that from the apparently unpromising stains (34 and 44 A) as a basis, very fine stains can be produced by (1) correct choice of the batch ingredient, (2) introduction of a small amount of alkali,* (3) decrease of the silica.

10. Use of selenium as a constituent of the stain and as a raw addition to the glaze. This oxide is known to give a very pleasing red tint.

11. Use of chromium-tin pink stains in various types of cone 010 glazes. A very interesting raw chromium-tin crystalline glaze was obtained at 010 in the Ohio State Ceramic Laboratories having the following molecular formula.

$$\left.\begin{matrix} 0.753\ PbO \\ 0.065\ K_2O \\ 0.180\ Na_2O \end{matrix}\right\} \left\{\begin{matrix} 0.06\ Al_2O_3 \\ 0.065\ Cr_2O_3 \end{matrix}\right\} \left\{\begin{matrix} 0.316\ SiO_2 \\ 0.1\ SnO_2 \end{matrix}\right.$$

ACKNOWLEDGEMENTS.

The writers desire to acknowledge their indebtedness to Professor Edward Orton, Jr., for permission to pursue

*R. H. H. Jones, Vol. I, p. 1, English Ceramic Society, states that alkalies are beneficial. This observation by Mr. Jones is in accord with the above.

and publish this investigation, as well as for his generosity and interest which made possible for exhibition purposes the mounting of the 540 trials on cloth bound cardboard.

DISCUSSION.

Mr. Plusch: What is the source of the calcium carbonate? I have found calcium flouride produced better reds than the calcium carbides.

Mr. Purdy: I found the same thing true with gypsum. By introducing calcium as gypsum, we produce a fiery, blood red, while with calcium carbonate it was considerably more of a brownish-red color.

Mr. Stover: As nearly all English recipes call for thoro washing and calcining, I think that would make some difference. In my own experience, I find I get much brighter effects by thoro washing and re-calcining. Oxidation and reduction of chromic stains in balls and fired in the open.

Mr. Will: As to the influence of washing on colors: In making underglaze colors, we tried other sources of chromium in order to do away with washing, but found we could not use the colors so produced and had to come back to bichromate and thoro washing to make sure of getting the same colors right along. As for lead chromate, I called for samples from different manufacturers and found some mixed with impurities as high as fifty or sixty per-cent. That might possibly account for the difference you obtained in the different lead chromate trials.

Mr. Burt: Were these washed?

Mr. Purdy: Neither washed nor calcined. Someone spoke earlier about burning color in open or reducing conditions. Better color has been obtained by reducing the stain at first, then permitting oxidation later.

Mr. Jackson: I would like to ask what you think is the influence of temperature upon the stain when first calcined? If calcined at cone 5, what would be the effect at cone 8?

Mr. Purdy: None, I would say, because in the factory where my first experience was gained, in chrome tin pinks, we had a cone 8 biscuit, cone 2 glost, and cone 4 biscuit, and it never made any difference into which of these the stains were calcined.

Mr. Jackson: What makes me ask that question is this: With a given type of stain and a given type of glaze, one is successful insofar as the high fire is given to the stain. After the first calcination, you will find there is a great difference in the amount of matter that comes off in the washing at the lower temperature and then at the higher temperature; and I have always thought that the higher temperature gave much the firmer combination to work with.

Mr. Walrath: I will ask what is the effect of boracic acid in the stain when used as a fritt?

Mr. Purdy: I never conducted a series of experiments to bring out that point. I have copied formulae that had boracic acid in and they gave fair results. I do not know what the effect of the boracic acid would be.

Mr. Will: The effect of boracic acid, in my experience, in the stain alone, has been in producing a lilac color.

Mr. Walrath: I ask that question because I have been told it was destructive to the color, and in my experience with color stains I have found the best color I produce is with the use of boracic acid.

Mr. Jackson: My experience has been, with a high lime content, to use high boracic acid; with low lime, low boracic acid.

Mr. Purdy: You mean in the stain.

Mr. Jackson: I mean in both stain and glaze.

Mr. Elcod: I have had some experience with what you call chrome-tin reds, called *Sang de boeuf*, the old copper red. If you fire chrome tin stain too hard in the calcining you lose the richness of the red tinge.

Mr. Purdy: You get a richer effect with a lower calcining of the stain?

Mr. Elcod: Yes. With a boracic acid lime glaze you get the best result.

Mr. Purdy: The variation in composition of the stain, then, is quite a factor from your experience?

Mr. Elcod: Yes.

Mr. Will: About six months ago, I made some investigations in chrome-tin pinks which showed that the difference in composition of the stain produced a proportionate difference in colors obtained. The difference was so clearly defined in the three series made that without looking at the numbers on the backs of the trials I could lay them out serially in accordance with their composition.

Mr. Purdy: Do you infer from that that the red is due to the formation of some compound, or to a physical precipitatin of the chromium?

Mr. Will: I think from the experiments I made it is to be directly traced to varying amounts of chrome.

A STUDY ON THE PRODUCTION OF OPALESCENCE IN HIGHLY ACID GLAZES WITH NOTES ON THE ACTION OF B_2O_3 WITH REGARD TO CRAZING.

BY

J. D. WHITMER, Willamina, Oregon.

Opalescence is a purely physical phenomenon similar to fluorescence. Search through a large number of references failed to reveal any data on the nature of opalescence except that it was due to the refraction of light. The phenomenon, as observed in glazes, seems to be due to the refraction of the light by particles of undissolved matter suspended in the glaze matrix. This refracted light has a decided bluish tinge which changes to a golden hue at certain angles of refraction.

While this phenomenon has been observed and commented upon by different investigators, so far as the writer is aware, no detailed study of it has ever been attempted. Consequently, the following investigation, based upon the work done by Prof. Purdy in fritted glazes as reported in Vol. IX of the transactions of the American Ceramic Society, was designed to study the production of the phenomenon.

GENERAL PLAN OF WORK.

In planning the work, the following references were found and consulted:

Vol. II of Seger's Works.

Transactions of the English Ceramic Society, 1904-1905.

Prof. Purdy's Fritted Glaze Studies, Vol. IX, Trans. Am. Cer. Soc.

The glazes reported as giving opalescence in these three references bore marked similarity. It was decided to follow Prof. Purdy's lead insomuch as he has touched upon the subject more fully than any of the others.

Adopting therefore, a fritted glaze as the type, it was found that four variations could be made as follows:

(1) Variation in the composition of the RO.

(2) Variation in the Al_2O_3 content, or variation in the basic oxygen ratio.

(3) Variation in the oxygen ratio of the glazes.

(4) Variation in the molecular ratio of B_2O_3 to SiO_2.

Inasmuch as only three variations are conveniently handled in one investigation, the following were decided upon:

(1) Variation in oxygen ratio, O.R.

(2) Variation in the B_2O_3 to SiO_2 ratio.

(3) Variation in the RO.

Prof. Purdy in his fritted glaze studies, pages 86 and 87, makes the following deductions:

(1) "Opalescent effects can be produced in a glaze by supersaturating it with SiO_2 at high oxygen ratios."

(2) "An O.R. of at least 1:4 seems to be requisite."

(3) "The presence of a certain equivalent amount of Al_2O_3 is also requisite ..... In the studies at hand, 0.20 equiv. Al_2O_3 ..... gave the best results."

(4) "That rather high B_2O_3 content was required and the higher the B_2O_3, the better the opalescent effects."

With the hope of gathering more proof for statements 1 and 2, it was decided to vary the O.R., overlapping Prof. Purdy's series and extending to the limit of commercially workable glazes.

For the same reason, it was decided to vary the molecular ratio of B_2O_3 to SiO_2, going far higher in B_2O_3 content than Prof. Purdy did in any of his series.

It was suggested to the writer that lime might have more influence in the production of the phenomenon than

Al_2O_3 and as Prof. Purdy had obtained some data upon Al_2O_3, it was decided to vary the RO rather than the Al_2O_3 content.

The RO.

As a basis for variation in the RO, the following was chosen as a well balanced and representative RO:

0.3 KNaO
0.3 PbO
0.4 CaO

CaO was varied at the expense of the lead, the variations being made by 0.1 equivalents.

The Al_2O_3.

Seger reports a glaze showing opalescence with 0.3 eqv. of Al_2O_3. In the English Transactions, an opalescent glaze carrying 0.33 eqv. Al_2O_3 was recorded. Prof. Purdy reports 0.2 eqv. as giving his best results. It was decided to follow Prof. Purdy's lead and use 0.2 eqv. in all of the glazes of this study.

The Oxygen Ratio.

The glazes referred to in the above paragraph have the following O.R. respectively:

Seger's, O. R. 1:3.63. English Trans., 1:3.5. Purdy, 1:4 and 1:4.5. It was deemed advisable to place the lower limit below any of these glazes, consequently an O.R. of 1:3 was chosen. From this, the O.R. was increased by increments of 0.5 eqv. up to 1:6.5, the latter limit being above any commercial glaze known to the writer. Seger has been reported to have used leadless barium fritted glazes with a ratio as high as 1:6 but we have gone one step higher in designing this series.

The Molecular Ratio.

The selection of the molecular ratios of B_2O_3 to SiO_2 was based upon facts gathered from the references already quoted. The glazes already referred to had an average ratio of 1:5, while Purdy stated that: "High B_2O_3 is re-

quired, and the opalescence here described not only does not appear unless the B_2O_3 is proportionately high, but it increases in intensity and is produced in wider and wider variation as the B_2O_3 increases in proportion to the SiO_2." His best results were obtained with a ration of 1 : 4.

In view of these facts, the lower limit of 1 : 5 was adopted and the upper limit was set at 1 : 6.5, the increments being 0.5 equivalent. Shown in tabular form, these three variations are as follows:

DIVISION INTO GROUPS BY OXYGEN RATIOS		DIVISION INTO GROUPS IN TERMS OF MOLECULAR RATIO OF B_2O_3 TO SiO_2		DIVISION OF SERIES INTO MEMBERS BY VARIATIONS IN THE RO.			
Group No.	O. R.	Series No.	B_2O_3 : SiO_2 Ratio	Member	KNaO	PbO	CaO
I	1: 3.0	1	1: 2.0	A	0.3	0.3	0.4
II	1: 3.5	2	1: 2.5	B	0.3	0.2	0.5
III	1: 4.0	3	1: 3.0	C	0.3	0.1	0.6
IV	1: 4.5	4	1: 4.0	D	0.3	0.0	0.7
V	1: 5.0	5	1: 5.0				
VI	1: 5.5						
VII	1: 6.0						
VIII	1: 6.5						

CALCULATING AND BLENDING.

The work of Prof. Purdy, as set forth by him in his Fritted Glaze Studies reported in Volume IX of the Transactions, was followed in this investigation. As Prof. Purdy has very clearly explained this process, it need not be repeated here.

FRITTING.

The following rules were observed in making up the fritts:

(1) All the RO was included.

GROUP No. 1

O. R. $\left\{ \begin{matrix} \text{O in acids} \\ \text{O in bases} \end{matrix} \right. = \frac{3}{1}$ Al_2O_3 Eqv.=0.2

Glaze No.	RO CONTENT.				SERIES 1 RATIO 1:2		SERIES 2 RATIO 1:2.5		SERIES 3 RATIO 1:3		SERIES 4 RATIO 1:4		SERIES 5 RATIO 1:5	
	K_2O	Na_2O	CaO	PbO	B_2O_3	SiO_2	B_2O_3	SiO_2	B_2O_3	SiO_2	B_2O_3	SiO_2	B_2O_3	SiO_2
A	.15	.15	.40	.30	.6857	1.3714	.60	1.50	.5333	1.60	.4364	1.7456	.3692	1.846
B	.15	.15	.50	.20	.6857	1.3714	.60	1.50	.5333	1.60	.4364	1.7456	.3692	1.846
C	.15	.15	.60	.10	.6857	1.3714	.60	1.50	.5333	1.60	.4364	1.7456	.3692	1.846
D	.15	.15	.70	.0	.6857	1.3714	.60	1.50	.5333	1.60	.4364	1.7456	.3692	1.846

GROUP No. 2

O. R. $\left\{ \begin{matrix} \text{O in acids} \\ \text{O in bases} \end{matrix} \right. = \frac{3.5}{1}$ Al_2O_3 Eqv.=0.2

Glaze No.	RO CONTENT.				SERIES 1 RATIO 1:2		SERIES 2 RATIO 1:2.5		SERIES 3 RATIO 1:3		SERIES 4 RATIO 1:4		SERIES 5 RATIO 1:5	
	K_2O	Na_2O	CaO	PbO	B_2O_3	SiO_2	B_2O_3	SiO_2	B_2O_3	SiO_2	B_2O_3	SiO_2	B_2O_3	SiO_2
A	.15	.15	.40	.30	.8000	1.6000	.7000	1.7500	.6222	1.8638	.5091	2.0365	.4308	2.1537
B	.15	.15	.50	.20	.8000	1.6000	.7000	1.7500	.6222	1.8638	.5091	2.0365	.4308	2.1537
C	.15	.15	.60	.10	.8000	1.6000	.7000	1.7500	.6222	1.8638	.5091	2.0365	.4308	2.1537
D	.15	.15	.70	.0	.8000	1.6000	.7000	1.7500	.6222	1.8638	.5091	2.0365	.4308	2.1537

(2) All the Al_2O_3 except 0.05 equivalent.

(3) All the SiO_2 except 0.4 equivalent.

These fritt compositions were somewhat unusual, but were adopted because of the unusual end in view.

The fritts were mixed thoroughly and melted in a gas-fired crucible fritt kiln. No difficulty was met with in melting them. All the fritts were practically insoluble in water. In order to prevent any loss from probable solubility, the water into which the fritts dropped was evaporated in shallow enameled iron pans. The same process was followed after grinding the fritts and glazes, so no change in composition was possible from this cause.

MATERIALS.

The following materials were used:

Borax, $Na_2B_4O_7$, $10H_2O$. Comb. Wt.	382
Boracic Acid (Granulated), B_2O_3, $3H_2O$. Comb. Wt.	124
White Lead, $Pb(OH)_2$, $2PbCO_3$. Comb. Wt.	258
Potassium Nitrate, KNO_3. Comb. Wt.	101
Calcined Aluminum Oxide, Al_2O_3. Comb. Wt.	102
Flint, (Ohio Silica Co), SiO_2. Comb. Wt.	60
Brandywine Feldspar. Comb. Wt.	697.4
Georgia Kaolin. Comb. Wt.	259.4
English Whiting. Comb. Wt.	99.06

The analysis of the feldspar, made in the laboratory of the Ceramic Department at the Ohio State University, was as follows:

SiO_2	70.93
Al_2O_3	16.00
CaO	0.78
K_2O	6.71
Na_2O	3.41
Loss on Ignition	0.65

The calculated molecular formula is:

$$\left.\begin{matrix}0.509\ K_2O\\0.392\ Na_2O\\0.099\ CaO\end{matrix}\right\}\ 1.12\ Al_2O_3\quad 8.43\ SiO_2$$

An analysis of the kaolin gave the following results:

SiO_2	47.38
Al_2O_3	39.57
H_2O	13.29
CaO	0.30
MgO	0.09

The calculated molecular formula is:

$$\left.\begin{matrix}0.004\ MgO \\ 0.014\ CaO\end{matrix}\right\} 1.00\ Al_2O_3\ \ 2.037\ SiO_2\ \ 1.904\ H_2O$$

The whiting analyzed as follows:

$CaCO_3$	97.00
Fe_2O_3 and Al_2O_3	0.41
SiO_2	2.54
	99.95

PREPARATION OF THE GLAZES.

The fritts were wet-ground, evaporated to dryness and the 8 weighed glazes were then made up and wet ground for one-half hour and passed through a 100 mesh screen. These were evaporated to dryness and again passed through a 100 mesh screen so as to be in the same physical condition. Blending was done in the dry way as described by Prof. Purdy.

THE BODY USED.

The body was biscuit white ware secured from the Mosaic Tile Co. of Zanesville. The composition of the body is not known to the writer. The tile were not as uniform in density as was desired, but answered the purpose fairly well.

PLACING OF TRIALS.

The trial pieces were set in small tile setters about 8 inches square, each setter holding 8 pieces. The location of each piece in each setter and the position of each setter in the kiln was noted and the same arrangement was kept throughout all burns, so that comparative results could be had.

BURNING OF THE GLAZES.

The glazes were burned in a small gas-fired test kiln in the department of Ceramics at the Ohio State University.

Four burns to temperatures of cones 05, 1, 5 and 10, respectively, were made which was thought to be a sufficient temperature range to mature all of the glazes.

These burns were pushed through rapidly and the cooling was accomplished in about 12 hours.

Cone 05 was reached after 8 hours firing.
Cone 1 was reached after 10 hours firing.
Cone 5 was reached after 11½ hours firing.
Cone 10 was reached after 14½ hours firing.

RESULTS OF BURNS.

The results of this investigation were somewhat negative in reference to opalescence and inasmuch as there is a large mass of data, it might be well to assemble the instances of opalescence.

Group I.

At cone 05, no traces of the phenomenon.

At cone 1, slight traces noticeable on the edges of member C, series 2 and 3.

At cone 5, some slight traces in member D of series 2.

Group II.

At cone 05, nothing resembling opalescence.

At cone 1, some indications along the edges of member D, series 2; members C and D, series 3.

At cone 5, slight opalescence in member D, series 1.

Group III.

At cone 05, opalescent effects in member B, of series 1, 2 and 3, series 1 showing the best results.

GROUP No. 3

O. R. $\left\{ \frac{\text{O in acids}}{\text{O in bases}} = \frac{4}{1} \right.$ Al_2O_3 Eqv.=0.2

Glaze No.	RO CONTENT.				SERIES 1 RATIO 1:2		SERIES 2 RATIO 1:2.5		SERIES 3 RATIO 1:3		SERIES 4 RATIO 1:4		SERIES 5 RATIO 1:5	
	K_2O	Na_2O	CaO	PbO	B_2O_3	SiO_2	B_2O_3	SiO_2	B_2O_3	SiO_2	B_2O_3	SiO_2	B_2O_3	SiO_2
A	.15	.15	.40	.30	.9143	1.8286	.8000	2.000	.7111	2.1277	.5818	2.3273	.4923	2.4614
B	.15	.15	.50	.20	.9143	1.8286	.8000	2.000	.7111	2.1277	.5818	2.3273	.4923	2.4614
C	.15	.15	.60	.10	.9143	1.8286	.8000	2.000	.7111	2.1277	.5818	2.3273	.4923	2.4614
D	.15	.15	.70	.0	.9143	1.8286	.8000	2.000	.7111	2.1277	.5818	2.3273	.4923	2.4614

GROUP No. 4

O. R. $\left\{ \frac{\text{O in acids}}{\text{O in bases}} = \frac{4.5}{1} \right.$ Al_2O_3 Eqv.=0.2

Glaze No.	RO CONTENT.				SERIES 1 RATIO 1:2		SERIES 2 RATIO 1:2.5		SERIES 3 RATIO 1:3		SERIES 4 RATIO 1:4		SERIES 5 RATIO 1:5	
	K_2O	Na_2O	CaO	PbO	B_2O_3	SiO_2	B_2O_3	SiO_2	B_2O_3	SiO_2	B_2O_3	SiO_2	B_2O_3	SiO_2
A	.15	.15	.40	.30	1.0286	2.0571	.9000	2.250	.8000	2.3915	.6545	2.6182	.5538	2.7692
B	.15	.15	.50	.20	1.0286	2.0571	.9000	2.250	.8000	2.3915	.6545	2.6182	.5538	2.7692
C	.15	.15	.60	.10	1.0286	2.0571	.9000	2.250	.8000	2.3915	.6545	2.6182	.5538	2.7692
D	.15	.15	.70	.0	1.0286	2.0571	.9000	2.250	.8000	2.3915	.6545	2.6182	.5538	2.7692

GROUP No. 5

O. R. $\left\{ \frac{\text{O in acids}}{\text{O in bases}} = \frac{5}{1} \right.$ Al_2O_3 Eqv.=0.2

Glaze No.	RO CONTENT.				SERIES 1 RATIO 1:2		SERIES 2 RATIO 1:2.5		SERIES 3 RATIO 1:3		SERIES 4 RATIO 1:4		SERIES 5 RATIO 1:5	
	K_2O	Na_2O	CaO	PbO	B_2O_3	SiO_2	B_2O_3	SiO_2	B_2O_3	SiO_2	B_2O_3	SiO_2	B_2O_3	SiO_2
A	.15	.15	.40	.30	1.1428	2.2856	1.000	2.500	.8889	2.6553	.7272	2.909	.6154	3.0768
B	.15	.15	.50	.20	1.1428	2.2856	1.000	2.500	.8889	2.6553	.7272	2.909	.6154	3.0768
C	.15	.15	.60	.10	1.1428	2.2856	1.000	2.500	.8889	2.6553	.7272	2.909	.6154	3.0768
D	.15	.15	.70	.0	1.1428	2.2856	1.000	2.500	.8889	2.6553	.7272	2.909	.6154	3.0768

GROUP No. 6

O. R. $\left\{ \frac{\text{O in acids}}{\text{O in bases}} = \frac{5.5}{1} \right.$ Al_2O_3 Eqv.=0.2

Glaze No.	RO CONTENT.				SERIES 1 RATIO 1:2		SERIES 2 RATIO 1:2.5		SERIES 3 RATIO 1:3		SERIES 4 RATIO 1:4		SERIES 5 RATIO 1:5	
	K_2O	Na_2O	CaO	PbO	B_2O_3	SiO_2	B_2O_3	SiO_2	B_2O_3	SiO_2	B_2O_3	SiO_2	B_2O_3	SiO_2
A	.15	.15	.40	.30	1.2572	2.5144	1.100	2.750	.9778	2.9192	.8000	3.200	.6769	3.3845
B	.15	.15	.50	.20	1.2572	2.5144	1.100	2.750	.9778	2.9192	.8000	3.200	.6769	3.3845
C	.15	.15	.60	.10	1.2572	2.5144	1.100	2.750	.9778	2.9192	.8000	3.200	.6769	3.3845
D	.15	.15	.70	.0	1.2572	2.5144	1.100	2.750	.9778	2.9192	.8000	3.200	.6769	3.3845

GROUP No. 7

O. R. $\left\{ \frac{\text{O in acids}}{\text{O in bases}} = \frac{6}{1} \right.$ Al_2O_3 Eqv.=0.2

Glaze No.	RO CONTENT.				SERIES 1 RATIO 1:2		SERIES 2 RATIO 1:2.5		SERIES 3 RATIO 1:3		SERIES 4 RATIO 1:4		SERIES 5 RATIO 1:5	
	K_2O	Na_2O	CaO	PbO	B_2O_3	SiO_2	B_2O_3	SiO_2	B_2O_3	SiO_2	B_2O_3	SiO_2	B_2O_3	SiO_2
A	.15	.15	.40	.30	1.3714	2.7430	1.200	3.000	1.0667	3.1830	.8727	3.4908	.7384	3.6922
B	.15	.15	.50	.20	1.3714	2.7430	1.200	3.000	1.0667	3.1830	.8727	3.4908	.7384	3.6922
C	.15	.15	.60	.10	1.3714	2.7430	1.200	3.000	1.0667	3.1830	.8727	3.4908	.7384	3.6922
D	.15	.15	.70	.0	1.3714	2.7430	1.200	3.000	1.0667	3.1830	.8727	3.4908	.7384	3.6922

GROUP No. 8

O. R. $\left\{ \frac{\text{O in acids}}{\text{O in bases}} = \frac{6.5}{1} \right.$ Al_2O_3 Eqv.=0.2

Glaze No.	RO CONTENT.				SERIES 1 RATIO 1:2		SERIES 2 RATIO 1:2.5		SERIES 3 RATIO 1:3		SERIES 4 RATIO 1:4		SERIES 5 RATIO 1:5	
	K_2O	Na_2O	CaO	PbO	B_2O_3	SiO_2	B_2O_3	SiO_2	B_2O_3	SiO_2	B_2O_3	SiO_2	B_2O_3	SiO_2
A	.15	.15	.40	.30	1.4857	2.9716	1.300	3.250	1.1556	3.4668	.9454	3.7816	.8000	4.000
B	.15	.15	.50	.20	1.4857	2.9716	1.300	3.250	1.1556	3.4668	.9454	3.7816	.8000	4.000
C	.15	.15	.60	.10	1.4857	2.9716	1.300	3.250	1.1556	3.4668	.9454	3.7816	.8000	4.000
D	.15	.15	.70	.0	1.4857	2.9716	1.300	3.250	1.1556	3.4668	.9454	3.7816	.8000	4.000

At cone 1, signs of opalescence noticeable in member C, series 1, but not as good as at the lower temperature.

At cone 5, some opalescence on edges of undissolved patches in member C and D of series 2. Slight traces in member D of series 3.

Group IV.

At cone 05, some slight traces in member B of series 1, 2 and 3, that in series 3 showing the strongest.

At cone 1, some opalescence but not strong in member B, series 3 and 4.

At cone 5, opalescent on edges of member C, series 1. Member B, series 2 has traces of it on edges of undissolved matter.

Group V.

At cone 05, opalescent tendencies, found in member B, series 3 and 4.

At cone 1, member B, series 1 and 2 give opalescent effects along the edges; member B, series 5 shows bluish tint of opalescence.

At cone 5, member B, series 3, C, series 2, and C and D of series 1, all have opalescence around edges of undissolved material.

Group VI.

At cone 05, traces of opalescence in member A, series 1, member B of series 3, 4 and 5.

At cone 1, slight traces in member A of series 2 and 3. Good effects in glaze B of series 5.

At cone 5, effects shown to a slight extent in member A of series 5 and member B of series 1 and 2.

Group VII.

At cone 05, traces in member A of series 1, also member B of series 5.

At cone 1, prominent effects in member A of series 1, 2, 3 and 4,—series 2 giving probably the best results.

At cone 5, member A of series 1, 2, 3, 4 and 5 shows some traces, with the best results in series 4 and 5.

Group VIII.

At cone 05, member A, series 1 gives a very nice opalescent effect; the same glaze in series 2 and 3 shows it but less pronounced.

At cone 1, member A of series 1, 2, 3 and 4 gives opalescence with series 2 and 3 showing best.

At cone 5, some effects in member A of series 1, 2 and 3. Series 2 gives best results but not as good as at cone 1.

DISCUSSION OF RESULTS.

As can be seen from the trials at hand and by the data assembled above, no good piece of opalescence was developed. Member A, series 1 of Group VIII developed the most perfect effect, but this was confined to one end of the tile where the glaze was exceedingly thick. In this piece, the undissolved matter was suspended in the glaze in a film of finely divided particles which gave a soft blue tint to the glaze. This glaze was very clear and bright, due to the high B_2O_3 content which permitted the easy refraction of light. Member B, series 5, Group VI was a very fair piece, the effect being scattered over the entire surface, but the surface was dull, which deadened the opalescent effect. In this piece, the pinholes appear as small wells of blue material which give a bluish tint to the glaze. This glaze is not as thick as the one first mentioned.

Most of the other instances mentioned above are confined to the edges of the trial piece or around the edges of the patches of undissolved matter.

It cannot be stated definitely where lay the failure of these glazes to develop opalescence, because from all indications they should have done so. Moreover, several of the

fritts gave promise of some very pretty effects. The fritts in the making oftentimes gathered in strings as they dropped into the water, cooled suddenly and gave beautiful instances of opalescence. The piece of fritt shown is an instance of some of the promising effects which did not materialize in the glazes.

CONCLUSIONS.

As has been stated previously, the work herein presented has been negative and no decided conclusions can be reached. However, there are a few things which the writer wishes to call attention to.

(1) It seems immaterial what may be the actual composition of the floating matter in the glaze matrix which refracts the light. It appears necessary that this material should be finely subdivided and evenly distributed throughout the glaze to produce the best effects. Heavy masses of undissolved matter will reflect the light, producing opacity, but the thin, filmy particles will refract the light, producing opalescence.

There is nothing to indicate what the actual composition of the particles producing opalescence may be, whether they are borates or SiO_2 separating out, or whether they are particles of undissolved lime. It was the intention to make a microscopic section of the piece of fritt shown but time prohibited this, consequently no light can be thrown on this phase of the subject.

(2) From observed data, it can be stated that the glaze coating should be as thick as possible. Wherever thick glaze coatings occurred, there opalescence seemed to develop more uniformly and to a greater degree of perfectness. These greater depths seem to lend substance and beauty to the phenomenon where thin glazes give it small chance to develop.

(3) High acidity appears to be a prime requisite to the development of the phenomenon in its maximum beauty. In this investigation, the largest number of in-

stances were had with a ratio of 1:6. Good effects were had with ratios of 1:5.5, 1:6 and 1:6.5. These ratios are remarkably higher than those quoted by Prof. Purdy. He states that a ratio of 1:4.5 gave the finest results, but nothing worth while was developed in these experiments at that acidity. The following glaze is Purdy's best:

$$\left.\begin{matrix} 0.126\ Na_2O \\ 0.124\ K_2O \\ 0.500\ CaO \\ 0.250\ PbO \end{matrix}\right\} 0.2\ Al_2O_3 \quad \left\{\begin{matrix} 2.6182\ SiO_2 \\ 0.6546\ B_2O_3 \end{matrix}\right.$$

O. R. 1:4.5

Comparing this with glaze B, series 4, Group IV, we have practically the same glaze with but a slight trace of opalescence at cone 1. At cones 5 and 10, the temperature at which Purdy's best results were obtained, nothing but clear glazes resulted. These variations are difficult to explain, as great care was exercised throughout the entire investigation. The only part of the whole experiment that could be criticized was the burning. It was the intention to make all burns on a certain schedule but the demands on the kiln were so great that it was found necessary to carry the burns through more rapidly than had been planned. The writer believes that the firing and cooling conditions are a very essential part in the development of opalescence and it is evident that the best possible conditions were not secured.

(4) The data on the $B_2O_3 : SiO_2$ ratio is not clear. Ratios of 1:3 or 1:4 seem sufficient. Higher ratios than these seem to have produced the greatest number of instances, but the lower ratios gave the best effects. The B_2O_3 lowers the maturing point of the glaze and makes bright glazes but it appears unnecessary to use a greater ratio than 1:4.

(5) The lime seems sufficiently high at .5 eqv. The best results were found in the glazes carrying .4 and .5 eqvs. Larger amounts of lime at the lower temperatures produced opacity and at the higher temperatures hung in

heavy white globs, the effect being somewhat like curdled milk.

(6) The best temperature range, judging from these experiments is from cones 1 to 5. At cone 10, no opalescence was produced, and at cone 05 only about one-half as much as at either cone 1 or cone 5. The actual temperature depends upon the composition of the glaze.

NOTES ON CRAZING.

Although the results as to opalescence were negative, the carrying through of these experiments brought to light some data on the action of B_2O_3 with reference to crazing which was thought well worth while mentioning at this time.

To facilitate ready reference and easy assimilation, this data is shown on 8 charts, each chart containing one group of glazes at the three temperatures used in this investigation at which crazing resulted. Referring to Chart No. 1, we see that this contains the data for Group 1. The lower block of rectangles represents the 20 glazes of Group I burned at cone 05; the next higher block, the same glazes burned at cone 1, etc. Temperature increments are therefore represented from bottom to top of the charts. The variation in the RO is represented from top to bottom of each block of glazes, the CaO increases while the PbO decreases from top to bottom. This same variation occurs in each block of glazes. The B_2O_3 to SiO_2 ratio varies from right to left of each block, the SiO_2 increases as the B_2O_3 decreases from right to left. The crazing on any single trial piece is shown by lettering in the rectangle representing that glaze. The relative amount being represented according to the following schedule:

(1) Very badly crazed, represents the worst crazing, very fine mesh.

(2) Badly crazed, coarser mesh than above but still bad.

(3) Crazed, having more than 15 to 20 craze marks but less crazed than in No. 2.

(4) Somewhat crazed, from 5 to 15 craze marks.

(5) Slightly crazed, from 2 to 5 craze marks.

(6) One craze mark.

(7) Blank spaces, no crazing. The cone 10 burn is not included on the charts as no crazing resulted at this temperature. With this explanation, the charts can be intelligently followed.

Effect of the $B_2O_3 : SiO_2$ Ratio.

What is the action of B_2O_3 upon the phenomenon of crazing? Two widely different opinions are held on this question and any further data seems well worth reporting. The present investigation may contribute some light:

Seger states explicitly that "Introduction of boric acid into a glaze as a substitute for silica decreases the coefficient of expansion;" also, "it follows that the coefficient of expansion of the glaze decreases with an increase of the boric acid content, and more decidedly than with an increase of silicic acid, and thus crazing can be lessened or stopped by an increase of the boracic acid content, or by a more extensive substitution of silica by boric acid."

Purdy, on the other hand, as a result of his experiments in fritted glazes already quoted, states in direct opposition to the above quotations from Seger, that "B_2O_3 increases the coefficient of expansion and contraction of a glaze, thus causing crazing."

Burt's experience, *Vol. VIII, Transactions American Ceramic Society,* seems to corroborate the observations of Purdy.

By referring to the 8 charts, the data obtained in this study may be followed. The two lower rows of glazes in each block on each chart are high in lime, 0.6 and 0.7 equivalents respectively and at the low boracic acid end of the group often become matt and immature. For this reason, it was thought no just comparison could be made

between these glazes at the extremes of high and low boracic acid, since the physical condition of a mature and immature glaze are radically different. Consequently, the high lime glazes, 0.6 and 0.7 eqv. are not considered in the following discussion.

There is no crazing at all at cone 10.

Chart 1.

Cone 05.

By comparing gazes having high $B_2O_3 : SiO_2$ ratios with those having low ratios, no appreciable difference in the relative amount of crazing can be found.

Cone 1.

At this temperature, member A remains practically unchanged throughout but member B shows a decrease in crazing with increase of B_2O_3. This lends a little strength to Seger's point of view.

Cone 5.

It will be noticed here that member A is about the same on the high and low B_2O_3 end but is slightly crazed in the middle series. Member B shows less crazing at the high B_2O_3 end. This favors somewhat Seger's view.

Chart 2.

Cone 05.

The evidenc here may be termed neutral as both members A and B are crazed about alike throughout the five series.

Cone 1.

It will be seen that at this temperature practically no difference is noticeable throughout the five series.

CHART NO. 1.

GROUP 1. O. R. = 1:3

Member	Series 5 Ratio 1:5	Series 4 Ratio 1:4	Series 3 Ratio 1:3	Series 2 Ratio 1:2.5	Series 1 Ratio 1:2
A			Slightly Crazed	One Craze Mark	
B	One Craze Mark	Slightly Crazed	Somewhat Crazed	One Craze Mark	
C			Slightly Crazed	One Craze Mark	
D					

Cone 5.

A	Crazed	Crazed	Crazed	Crazed	Crazed
B	Badly Crazed	Crazed	Crazed	Slightly Crazed	Somewhat Crazed
C	Badly Crazed	One Small Craze Mark	Somewhat Crazed	Somewhat Crazed	Slightly Crazed
D	Immature, Badly Crazed	Opaque, Slightly Crazed	Opaque, Somewhat Crazed		

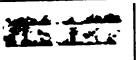
Cone 1.

A	Very Badly Crazed	Very Badly Crazed	Very Badly Crazed	Very Badly Crazed	Very Badly Crazed
B	Matt, Very Badly Crazed	Very Badly Crazed	Very Badly Crazed	Very Badly Crazed	Very Badly Crazed
C	Matt, Very Badly Crazed	Matt, Badly Crazed	Opaque, Badly Crazed	Opaque, Badly Crazed	Opaque, Badly Crazed
D	Immature, Badly Crazed	Matt, Badly Crazed	Matt, Badly Crazed	Opaque, Badly Crazed	Opaque, Badly Crazed

Cone 05.

CHART NO. 2.

GROUP 2. O. R. = 1 : 3.5

Member	Series 5 Ratio 1 : 5	Series 4 Ratio 1 : 4	Series 3 Ratio 1 : 3	Series 2 Ratio 1 : 2.5	Series 1 Ratio 1 : 2
A					
B				One Craze Mark	Slightly Crazed
C					
D					

Cone 5.

A	Crazed	Slightly Crazed	Somewhat Crazed	Somewhat Crazed	Somewhat Crazed
B	Somewhat Crazed	Somewhat Crazed	Somewhat Crazed	Slightly Crazed	Somewhat Crazed
C	Crazed	Slightly Crazed	One Craze Mark		Slightly Crazed
D	Matt, Crazed				

Cone 1.

A	Very Badly Crazed	Badly Crazed	Very Badly Crazed	Very Badly Crazed	Very Badly Crazed
B	Matt, Very Badly Crazed	Very Badly Crazed	Very Badly Crazed	Very Badly Crazed	Badly Crazed
C	Immature, Crazed	Matt, Very Badly Crazed	Opaque, Very Badly Crazed	Opaque, Very Badly Crazed	Opaque, Badly Crazed
D	Immature, Crazed	Matt, Badly Crazed	Matt, Badly Crazed	Opaque, Very Badly Crazed	Opaque, Badly Crazed

Cone 05.

CHART NO. 3.

GROUP 3. O. R. = 1:4

Member	Series 5 Ratio 1:5	Series 4 Ratio 1:4	Series 3 Ratio 1:3	Series 2 Ratio 1:2.5	Series 1 Ratio 1:2
A				Slightly Crazed	
B					
C					
D					

Cone 5.

A	One Craze Mark	Slightly Crazed	One Small Craze Mark	One Craze Mark	Slightly Crazed
B		One Craze Mark			Slightly Crazed
C	One Craze Mark				Slightly Crazed
D					

Cone 1.

A	Badly Crazed	Crazed	Crazed	Badly Crazed	Crazed
B	Matt, Crazed	Crazed	Crazed	Badly Crazed	Badly Crazed
C	Matt, Crazed	Matt, Crazed	Opaque, Crazed	Opaque, Crazed	Badly Crazed
D	Immature, Slightly Crazed	Matt, Somewhat Crazed	Immature, Crazed	Opaque and Immature, Crazed	Opaque, Crazed

Cone 05.

CHART NO. 4.

GROUP 4. O. R. = 1 : 4.5

Member	Series 5 Ratio 1 : 5	Series 4 Ratio 1 : 4	Series 3 Ratio 1 : 3	Series 2 Ratio 1 : 2.5	Series 1 Ratio 1 : 2
A					
B					
C					
D					

Cone 5.

A			Slightly Crazed	One Craze Mark	
B					One Large Craze Mark
C					
D					

Cone 1.

A	Somewhat Crazed	Crazed	Crazed	Somewhat Crazed	Badly Crazed
B	Matt, Somewhat Crazed	Somewhat Crazed	Crazed	Opaque, Somewhat Crazed	Crazed
C	Matt, Somewhat Crazed	Matt, Somewhat Crazed	Crazed	Opaque, Somewhat Crazed	Crazed
D		Matt, One Craze Mark	Immature, Crazed	Immature, Crazed	Immature, Crazed

Cone 05.

CHART NO. 5.

GROUP 5. O. R. = 1 : 5

Member	Series 5 Ratio 1 : 2.5	Series 4 Ratio 1 : 4	Series 3 Ratio 1 : 3	Series 2 Ratio 1 : 2.5	Series 1 Ratio 1 : 2
A					
B					
C					
D					

Cone 5.

A		One Craze Mark		One Craze Mark	
B					
C					
D					

Cone 1.

A	Slightly Crazed	Somewhat Crazed	Somewhat Crazed	Somewhat Crazed	Crazed
B	One Craze Mark	Slightly Crazed	Opaque, Somewhat Crazed	Opaque, Somewhat Crazed	Opaque, Somewhat Crazed
C		Slightly Crazed	Opaque, Somewhat Crazed	Opaque, Somewhat Crazed	Opaque, Somewhat Crazed
D				Immature, Badly Crazed	Immature, Crazed

Cone 05.

CHART NO. 6.

GROUP 6. O. R. = 1 : 5.5

Member	Series 5 Ratio 1: 5	Series 4 Ratio 1: 4	Series 3 Ratio 1: 3	Series 2 Ratio 1: 2.5	Series 1 Ratio 1: ?
A					
B					
C					
D					

Cone 5.

A	One Craze Mark		Slightly Crazed		
B					
C					
D					

Cone 1.

A	Somewhat Crazed	Somewhat Crazed	Somewhat Crazed	Somewhat Crazed	Somewhat Crazed
B		Slightly Crazed	Opaque, Somewhat Crazed	Slightly Crazed	Somewhat Crazed
C		Opaque, Somewhat Crazed	Opaque, Crazed	Opaque, Somewhat Crazed	
D				Immature, Badly Crazed	Immature, Badly Crazed

Cone 05.

CHART NO. 7.

GROUP 7. O. R. = 1 : 6

Member	Series 5 Ratio 1 : 5	Series 4 Ratio 1 : 4	Series 3 Ratio 1 : 3	Series 2 Ratio 1 : 2.5	Series 1 Ratio 1 : 2
A					
B					
C					
D					

Cone 5.

A					
B					
C					
D					

Cone 1.

A	One Small Craze Mark	Crazed From Blow			Slightly Crazed
B					One Craze Mark
C				Slightly Crazed	
D					

Cone 05.

CHART NO. 8.

GROUP 8. O. R. = 1 : 6.5

Member	Series 5 Ratio 1 : 5	Series 4 Ratio 1 : 4	Series 3 Ratio 1 : 3	Series 2 Ratio 1 : 2.5	Series 1 Ratio 1 : 2
A					
B					
C					
D					

Cone 5.

A					
B					
C					
D					

Cone 1.

A					One Small Craze Mark
B					
C					
D					

Cone 05.

Cone 5

At this temperature, the small amount of crazing is found in the highly borated glazes, hence tending to support Purdy's statement.

Chart 3.

Cone 05

Here the crazing seems about evenly balanced between the high and low borated glazes.

Cone 1

But little difference is observed at this temperature but what little there is may be added to the support of Prof. Purdy.

Cone 5

The single crazed glaze at this temperature is found in the second highest B_2O_3 series.

Chart 4.

Cone 05

Every glaze is crazed and the crazing seems evenly distributed.

Cone 1

At this temperature, what crazing there is will be found in the highly borated series.

At cones 5 and 10, no crazing.

Chart 5.

Cone 05

All the glazes considered are crazed and the crazing seems to be somewhat worse with the higher B_2O_3 content.

Cone 05

But two glazes have crazed and these are equally balanced with reference to the B_2O_3 content.

Cone 5, no crazing.

Chart 6.

Cone 05

All but one of the glazes considered are crazed and there seems to be no difference in the amount from low to high B_2O_3. The one uncrazed glaze is in the low B_2O_3 series.

Cone 1

Two crazed glazes; one in the low borate series, the other in the second highest.

Chart 7.

Cone 05

The glaze marked "crazed from blow" was uncrazed until struck. The other crazed glazes seem to add weight to Purdy's statement.

Chart 8.

Cone 05

One small craze mark is found on member A of the high borate series.

SUMMARY.

Summing up the results, we find that a greater number of instances support Purdy's view than Seger's, but that there are just as many instances which support neither Purdy nor Seger, or, in other words are neutral.

On the whole, the evidence does not seem positive nor conclusive enough to warrant any strong statement as to the actual status of B_2O_3. From these data, we should hesitate to confirm Prof. Purdy's conclusion. On the other hand, within the limits of the $B_2O_3 : SiO_2$ ratios used in this study, we would conclude that an increase of B_2O_3 at the expense of the SiO_2 for the purpose of lessening or curing crazing cannot be justified. Rather would we increase the total oxygen ratio, vary the RO or increase the firing temperature, all of which serve the purpose of lessening crazing.

It is to be remembered that the $B_2O_3 : SiO_2$ ratios used in this investigation are unusual and for the greater part, higher in the B_2O_3 content than those used by Prof. Purdy. It is possible that there is a certain limit to the amount of B_2O_3 that will have an effect on crazing and that this limit has been passed. Furthermore, it must be remembered that the body used was not of uniform density consequently some variation can be attributed to that source. It would have been better had absorption tests been run on all trial pieces and those outside of certain limits been rejected. But notwithstanding the shortcomings it is hoped that the data here presented will add something to what has been published heretofore and that it will be an incentive to further experimenting.

DISCUSSION.

Mr. Ashley: Mr. President, it does not have any very close connection to this paper, but I may say that after the paper on Fritted Glazes by Mr. Purdy came out in the *Transactions* I hunted up the mixture given by him which most closely agreed with the glaze being used by the pottery with which I was connected, and found his description of the properties of that glaze very closely coincided with the properties of the glaze we were using. Consequently, it strengthened my faith in the accuracy of his conclusions.

Mr. Binns: Mr. President, I am not prepared to discuss this paper with its wealth of information, but there is one question which occurs to me as to the purpose of producing an opalescent glaze. I was wondering if the idea underlying this investigation was the production of a glaze appearing opalescent when put on the ware. I am not sure, apart from the scientific nature of the investigation, that we are going to get any profitable effect if we can produce an opalescent glaze. The effect of the opal needs transmitted as well as refracted light to bring out these qualities.

Mr. Orton: The object of the investigation was to make use of opalescence as a mode of decoration. Instances have come to my attention where that phenomenon has been used most effectively. I have in mind as opalescence what Professor Purdy had in his mind when describing opalescence in his paper two years ago. I have seen instances of a very beautiful bluish haze over the glazed surface of the wares used as a decoration. This haze is not a surface phenomenon, nor due to any tangible or identifiable film on the surface. It seems to have the capacity to make the decorations underneath this glaze appear hazy and soft, giving a very high artistic value to the piece treated, especially where the painting beneath is a landscape, representing distances. I have seen some pieces of pottery which I would much like to own, where the beauty chiefly came from that delicate fogging of the glaze.

Mr. Binns: You are not referring to "vellum" ware?

Mr. Orton: No, nothing like "vellum" ware.

Mr. Stover: Were they not all curved surfaces, rather than flat, as you saw them?

Mr. Orton: On one piece which I have in mind, the opalescence began on the neck of the vase and followed the swell two-thirds of the way to the bottom.

Mr. Stover: The reason I ask the question is that I had in mind the opalescence of a soap bubble; and I wondered if some of these glazes on the flat surfaces would not have shown a greater amount of opalescence if they had appeared on curved pieces.

Mr. Orton: Mr. Purdy's trials, from which his conclusions were taken, were flat.

Mr. Binns: I am not quite clear what you are driving at, and I think there is some confusion as to the term "Opalescence". Mr. Stover speaks of the opalescence of a soap bubble. That is not opalescence, but iridescence. Opalescence needs the play of light which a semi-opaque body would not give, and it would not be a commercial

possibility at all for that reason. I have been wondering whether you are not confusing opalescence, giving the fire of the opal by transmitted light as expressed by those semi-transparent opalescent light globes, and mere milkiness. So I have wondered whether what is sought for by this investigation would be of any practical decorative value if secured, and I am not yet clear on that point. What is meant by opalescence is not clear, and it is not certain if we did succeed in getting it on a white ware body whether anything would be gained.

Mr. Burt: I would like to ask Professor Binns, in regard to the question he has raised as to a distinction between opalescence and iridescence, agreeing that iridescence is largely the result of surface reflection, isn't the other the same only produced at a little lower surface, due to the fractured surfaces reflecting the light, whereas the iridescent effect, as the appearance of coal oil on water, is surface reflection? I think it is merely a question as to whether the reflection of light is from the surface or from a depth of a minute fraction of an inch below the surface.

Mr. Orton: It seems to me that Mr. Burt is right in the main. The difference is mainly due to where the light is broken up, whether close to the surface, as in the pearl, or more deeply as in the opal. No doubt the opal has its beautiful fire from the latter cause, deep-seated fractures. But the thing which I have in mind, to which I have referred as opalescence, and which I have heard referred to by that title by many different persons, is neither a surface phenomenon nor a fracture. I would like to suggest that it may be due to the suspension of minute particles, crystalline matter probably, in and beneath the surface of the glaze, by which the light is reflected out again. The light ray goes in, hits the white body beneath and as it is refracted back out, passes through these particles, so that we get the effect of a prism, in the dissociation of the crystalline white light. If we have immensely fine crystalline matter suspended in the glaze, why wouldn't it have

the power to break up light which other crystals have? My own observations along this line have been limited, but I have seen cases where one piece of glass was milky and opaque at one end, and perfectly clear at the other, shading from one condition to the other with a most beautiful and enticing transition line of opalescent nature. I remember Mr. Burt giving me a piece of glaze fritt produced at Rookwood, which showed that transition line beautifully. The object of this investigation was really to produce a glaze with sufficient amount of suspended matter to give this effect.

Mr. Plusch: That reminds me that I took some ordinary clear glaze and added five to twenty-five per cent of (KNO_3—249, ZnO—233, SiO_2—419, TiO_2—99) fritt, and always got that iridescence. That was on flat tile, some set flat and some on end. That was probably from the crystalline particles of the fritt used.

Mr. Binns: In glass manufacture we expose the surface of the glass to various chlorides and produce different colors. In porcelain the same thing has been done by leaving a small opening at the bottom of the muffle door, and at the right temperature introducing a shovel with salts which would volatilize in the kiln. This produced iridescence on the glaze, but it was not of commercial value for the reason that it was not sufficiently visible.

Mr. Elcod: Iridescent glass or glaze is secured, when the glaze or glass contains some few per cent of silver oxide, besides bismuth, cobalt or uranium, etc.—and reduced in a muffle kiln, just below its deforming (glass) heat,—at about cone *022*.

I have made with about 2 per cent silver oxide, and according to the color wanted, with some other oxides, some brilliant iridescent lead-borosilicate glasses.

By putting 1.5—2.5 per cent oxide of silver in colored matt glazes for pottery and for tiles and after reducing them in a muffle kiln for about 10 minutes at cone *022*, I have also secured very nice iridescent effects.

By using bismuth, cobalt or chromium, besides silver, the lustrous effect is easier obtainable.

Other kind of iridescency is made on pottery or on glass, by fuming tin salts in the muffle kiln, at about cone *022*. The tin chloride can be also mixed with water and molasses, and can be blown on with an aerograph, on the finished glass goods, at the working hole—and a nice iridescency is secured by this means also.

Mr. Stover: I think one reason is probably the explanation given by Professor Orton, viz., a crystalline effect underneath the surface of the glaze, the rays of light passing through the smooth, outer surface, being broken up and passing back to the eye at different rates of speed, as explained by Ashley in Vol. VII. That is the reason I spoke of the soap bubble. Those flat tile seem to show that a curve is not necessary.

Mr. Orton: I had hoped there would be an energetic discussion of this crazing phenomenon. If not, I want to dissent from what Mr. Burt has said, viz., that Mr. Whitmer's data left the subject as it was before. We have the statement of Prof. Seger that a certain thing takes place, and one from Prof. Purdy that the opposite takes place. This Whitmer data seems to show that no marked tendency in either direction exists. Of course, we cannot base any final statements on any single series like this. The ground would have to be covered many times, before we could make a broad and final assertion that boric acid does or does not decrease the coefficient of a glaze. So far as this data is concerned, it would seem to prove that neither one of those statements is true, and that B_2O_3 does not affect the coefficient of expansion strongly one way or the other.

Mr. Bowers: It has been my experience in thick glazes that boric acid is neutral. If we want to produce crazing we would substitute soda and produce it immediately. I think those results are physical, not chemical.

The substitution of soda for borax in the thicker glaze will produce crazing immediately.

Mr. Plusch: That would simply tend to prove that the boric acid was acting as an acid content instead of an alkali. I do not see how you can compare Prof. Purdy's statement with Seger's. They were working along different lines. I do not think we could arrive at any definite law unless we would have all the features that entered into the final result tabulated, so as to look at it from every standpoint.

Mr. Binns: Since, Mr. President, Prof. Orton challenges us to discuss crazing, he opens a door which it may be somewhat difficult to shut. My own conclusions, or rather the evidence which has passed before me hitherto, has tended to show that it depends on the conditions under which we are working. I think I was able to show two or three years ago that boric acid sometimes increased the tendency to craze. I formulated at one time two theories. One was that a lead glaze could drink up silica from the body and thus could satisfy itself and cure its own tendency to craze, and the other that boric acid did not have such a power. Whether that is correct, I am not now prepared to say.

Mr. Ashley: I expected to hear Prof. Binns say that as boric acid is a base, if you increase boric acid and decrease the silica, you increase the crazing; or you decrease the boric acid, and increase the silica, you prevent crazing. As he did not touch that point, I will remind him of it.

I made some experiments myself, which are not in shape to communicate, using an earthenware glaze, keeping all other constituents of the formula the same and increasing the boric acid. In such cases, each increase of boric acid caused an increase of crazing.

Mr. Binns: Mr. Ashley offers another challenge. I have presented that subject to the society and as the society so far has not said anything on the other side, I am waiting. My own conclusions are unchanged.

SOME FALLACIES AND FACTS PERTAINING TO GLASS MAKING.

BY

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As indicated by the topic of this paper, it shall be my endeavor to present to the Society some of the fallacies that are so prevalent in the manufacture of glass articles and window glass as to substantially control not only the production, but the quality and the economic factors which enter into and govern the production and sale of glass in any form.

Permit me to first invite your kind attention to a short resumé of the manufacture of glass. Glass has been produced, according to the historians, since five or six thousand years B. C. As to what originally led to the making, or the discovery, of glass is not definitely established, but it is attributed to the Phoenicians. Although there may be some question as to the authenticity of the origin of its discovery, it is not at all improbable that this product was first made by the fusion of alkaline sands. Glazing has been found to exist in many of the products which it is claimed are relics of the efforts put forth at manufacturing three or four thousand years B. C., and also numerous of the primeval articles closely resemble glass. The fragments of such articles indicate, however, that they are not true glass, but are composed of the silicates of alumina, soda, lime and iron, alumina predominating in nearly all instances, which would indicate more or less argillaceous material being mixed with the raw materials used in the composition of this glass.

In a general way, the utility of flint, copper, clay and glass was discovered during about the same period, the

flints being used by a people at the same time as copper tools in the fourth and twelfth dynasties. It would appear that glazed pottery followed close upon the use of copper, because of the fact that most of the early pottery glazing indicates by its tinge that it was colored with copper salts, and investigation shows a considerable amount of copper in the specimens analyzed.

About 1300 B. C., or perhaps somewhat prior to this time, in the tombs of Beni Hasson are found articles of blown glass, as also were there found the remains of crucibles for melting glass, made of clay, and fourteen inches in diameter, some being found with glass in them. There were also discovered in these tombs, pictures of men blowing in the fire through metal pipes, and manipulating something upon the ends of these pipes, and these are supposed to depict the early glass worker.

It would seem that there has been little, or no progress in the art of producing glass articles for nearly 3200 years. We are substantially doing today what was done in those prehistoric times, for the manufacture of nearly all articles of glass is carried on in about the same manner, only perhaps on a larger scale, and possibly under somewhat more economic conditions, i. e., placing the raw materials in a clay receptacle, submitting same to the action of fire, and gathering upon the ends of metal pipes a quantity of the viscous metal, and blowing, or forming, same into the desired shapes.

Only within the last few years has there been any evident departure from this ancient and antiquated method of manufacture, and even today it is difficult to convince the average manufacturer that first quality and uniform metal can be produced in any other type of furnace than the pot furnace. Of course we have no determinative information as to what extent, or by what means, the Phoenicians carried on the manufacture of glass, or as to how extensive was their knowledge of economic productions and definite compounding of materials to pro-

duce glass, but it is safe to say that there has been but little progress in the actual knowledge of definite compounding of these materials, although it is one of the greatest factors to be considered today in the production of all articles of glass ware.

I believe that the average manufacturer has but a vague knowledge concerning the elements which enter into the making of a given quality of glass. As a matter of fact, there are a great many glass makers today who are absolutely ignorant of the components of glass, and I believe that I do not err when I say that a large majority of them believe that glass is composed of sand which has been brought to a molten condition, and that the other ingredients which they put in their batch have been carried away by the action of the heat.

So far as I have been able to learn (outside of one or two Germans and Frenchmen) there has been little or no scientific work conducted, or conservative investigation made, as to the definite qualities and properties produced by varying the quantities of elements constituting glass. We take any quantity of sand, lime, either in the form of calcium carbonate, oxide or hydroxide; soda, in the form of caustic soda, sodium carbonate, or sulphate, and perhaps varying quantities of magnesium carbonate or oxide together with such impurities as may exist in the form of aluminum, iron in its different oxides, oxides of cobalt, nickel, copper, chromium, titanium, barium, strontium and lithium. In the composition of our optical glasses, and glass having a high refractive index, there is added the oxides of lead, zinc, cadmium, bismuth, antimony, tin and arsenic. Then again we have those elements that produce certain color effects, such as copper, manganese, chromium, cobalt, nickel, gold, selenium, uranium, vanadium, iron, silver and alumina, although the definiteness of the color that may be produced by any of them is very problematic. It must be acknowledged, therefore,

that within the category of glass making lies a fair percentage of all of the elements with which nature has provided us.

Before attempting to describe the effects produced by any of the elements enumerated above, let us first consider the question of glass, or perhaps I might better say, permit me to first give my hypothesis of what it is, inasmuch as this subject has been discussed by but a few men, and these few have arrived at no definite understanding, and while I can give no absolute information as to the actual structure or composition of glass, I have a theory. It is maintained by many (and some good authorities) that it is an amorphous body, but by others that the term amorphous is an improper one. Although I have not heard the opinion expressed, I am of the belief that it can not be termed, strictly speaking, amorphous, but is isomorphous, that is, it is not what the literal interpretation of the word implies. I believe I have proof that it is practically impossible, at least in our present day method of manufacture, to produce a piece of amorphous glass, or rather, to produce a piece of glass which is all amorphous.

I have taken and examined photomicrographs of etchings made from glass, in which it is almost impossible to find an area larger than a few fractions of an inch in which there could not be found distinct, definite crystalline indications. On examination of an etching, or a piece of glass whose surface has been removed by means other than a mechanical one, it will be found that when sufficiently magnified, and the surface observed in a polarized or white light, there will be seen what might be called cells or drops in the form of nodes, and on which there are minute crystals, or at least some form of light depolarization, and this takes place uniformly and definitely where there is uniform composition and arrangement. Heat this specimen to 600° C, and it will, on cooling, show a different arrangement; pass ultra-violet, or sun light, through it for a long period of time, and it will further change at ordi-

nary temperature, but mechanical stress appears to have little or no effect on this arrangement.

Is it too preposterous to suppose that these nodes are drops or masses of liquid crystals, or have been such while in the molten state? Can we have a solid solution which has dissolved a part of these constituents, and those being the most active? If this is not the case, why, and how, does sunlight and ultra-violet light have an effect, an instance which is particularly more apparent in plate glass in which manganese and arsenic are used? I have seen perfectly white glass placed in a window sash on the south side of a building, and two years afterward this sheet of glass was a straw yellow. There must have been some molecular action to have caused this change of color, and how this could occur in a hard, solid substance like glass, without the existence of some more or less mobile properties, is not explained satisfactorily.

In the making of glass, the different ingredients are forced into a more or less complex and varied combination by heat, and, inasmuch as all things are either liquid, solid, or gaseous, according to their temperature, and the viscousness of semi-liquid or liquid bodies is a factor of its temperature, it would seem reasonable that in a material like glass, which has no definite point of liquification, the same laws would apply as to all other semi-liquid or saturated solutions, and the theory of osmotic pressure, surface tension, solid solution and liquid crystals could appropriately be applied to glass.

In my opinion, glass passes through all of the transitory stages of physical phenomena, and is influenced by the degree of action of all the phenomena known to science, but it is a very difficult matter to study their changes because of its transparent properties.

If a deep etching be examined by the microscope and magnified about 180 times, it will be seen that the field has the appearance of a honey comb, or is a cell-like structure, irregular in form, but it will be more irregular and

unequally attacked by the etching medium where any of the cells are of a different composition. The space between the cells is of a sea-green color, and is sufficiently pronounced to sharply define the size and shape of the cells. It has been observed that where the cell is fairly uniform, the physical properties of the glass were excellent. Some experiments conducted with an etching made on a sample of window glass which was taken from the product of a tank factory, disclosed the fact that heating and cooling produced less strain, and this metal worked more uniformly than any previous or subsequent samples; also, that the glass at this time was less susceptible to temperature changes than at any other time.

On an etching made on a salt-cake glass, at a time when the working of the metal was very unsatisfactory, and when the slightest change in the manipulation, or the exposing of one side of the lump gathered to a different temperature from the other, would invariably produce a cord, or wave, it was found that the cells were very irregular in shape and size, and that in several places there were indications that the cell envelope had been ruptured and crystals were forming, whereas in the previous instance there were no such indications, and the cells were fairly uniform in size and shape.

The following approximate analysis of these two glasses are substantially the same, and it will be noted that they show little or no difference in composition:

	No. 1	*No. 2*
SiO_2	72.14	72.21
CaO	12.84	12.81
Na_2O	13.21	13.29
MgO	.31	.32
Al_2O_3	1.27	1.20
Fe_2O_3	.18	.18
	99.95	100.01

From this two lines of argumentation may be followed, viz., that if the analysis is sufficiently accurate, then very slight changes in composition are far more effective

than a general conclusion would indicate as being practical to control. Secondly, that it is not so much a matter of chemical composition as of chemical and chemico-mechanical *combination*. It is my opinion that the latter is the essential factor which effects quality of product, and that glass is a compound mixture of silicates, combined in certain definite proportions according to temperature, the aggregate of chemical composition being mechanically combined by cohesion and adhesion. That at all temperatures glass is susceptible to internal chemical and mechanical changes, which can be accounted for only by the liquid crystal theory and presumption of a solid solution.

It will appear evident to anyone who may have the opportunity of studying the making of glass as practiced in America, that there is no consistency of opinion among manufacturers or superintendents as to the proper method of carrying out the various steps in the process of mixing, melting, working, annealing and cutting glass. That which one man will declare is absolutely ruinous to his product and method, another will strongly maintain to be a vital essential to his production.

One of the largest concerns in this country will absolutely refuse to accept, or endeavor to use, a lime which carries more than 3% of magnesia, while another concern, whose reputation for quality stands unexcelled, has for years been using a lime carrying an average of 6% magnesia, and at times going as high as 13%. This same concern, however, will not use anything but a pure, double-washed sand carrying less than 1% alumina, while one factory is using an unwashed sand carrying about 6% alumina, and at other plants they are using sand of about 3%, but, strange to say, the factory using the 6% are "top notchers" in production of quantity and quality.

Another party thinks that arsenic in the batch is absolutely essential, while others claim that it is a detriment, and cryolite should be used; yet those that use neither are making as good glass as either of the others. One

claims that nitre must be added to the batch to get his color, while another says it destroys the surface and does not affect the coloring; however, I doubt if either one could tell by the finished product, or the melting, whether there was nitre in the batch or not.

One concern cannot melt without from one to two pounds of gas pressure on the burners, whereas another uses but two ounces. One will claim that they can use nothing but Pennsylvania coal in their producers, while another will say that it is an impossibility to use same, because this coal has a tendency to make cordy glass. Some claim that Indiana coal, or Texas oil, burned in lehrs will sulphur glass, while others consider that this contention does not comply.

And so on, I could mention instances of apparent paradoxical operation for nearly every process in the industry. As a matter of fact, glass, as it is found in the market today, is made up of almost an unlimited number of ingredients and combination of the elements, and by as many different methods of operation, the details of which are little understood.

What effect varying proportions of the different elements have on the physical and chemico-physical properties of glass, we have but a meagre knowledge from a scientific standpoint, and none in a practical way. I have had an opportunity of studying some of the effects produced by altering or introducing various materials in glass, and while I can see now where I might have improved the use of them and obtained much greater results, I at that time was more or less inclined to accept the statements of the pioneers in the business as facts, and I am convinced that they believed them to be facts, based on repeated and long experience. However, mere reliance on the statements of any one as a basis for scientific reasoning to determine the cause or effect of any change in conditions, was soon found to be impossible, for, as illustrated above, no two would agree as to constituency or method, and, obviously, there was no base on which either side

could build a logical determination that would work out from all directions, or that could not be refuted by the other fellow. Consequently I started working out my own theories on some of the more radical ones, with the result, I confess, that I did not get far toward proving or disproving my own hypothesis. I did, however, conclusively determine one very important factor in any process, or manipulation, and that is the important influence exerted by many of the supposedly inconsequential details, which are usually either entirely disregarded, or considered of minor importance.

I found that glass making today is carried on with no regard to definite proportions or consistent methods of operation; that it is void of any *true* knowledge, and is essentially an industry based and operated upon and subservient to personal opinions and prejudice, poisoned by legendary ideas and jealousies, and made generally unwholesome by lack of progressiveness or any initiative on the part of those who might, if they would, arise from this quagmire and put themselves on a basis of scientific fact.

Glass making is different from most any other metallurgical operation, it being a process of synthesis while nearly all others are of analysis. By this synthesis we are supposed to produce a material which will transmit light so perfectly as to produce no distortion of color to objects viewed through it, and this calls for absolute refractive indices, homogeneous composition, and perfect mechanical arrangement.

An attempt to incorporate in this paper more than the most important conclusions and facts found by these investigations, would be impractical; therefore I will confine myself to those established facts which are vital to production of quantity and quality, and which have been found to be subjects of diverse opinions among practical men.

That which is the greatest cause of discussion, praise, condemnation, secrecy, jealousy, prejudice, and *imaginary*

troubles is the "batch" or mixture of ingredients which go to make up the final product, and which we will consider in the order of their importance, namely — Sand, Lime, Soda, Clarifying, Decolorizing or Coloring Agents, and Carbonizing or Deoxidizing Agents.

SAND.

I have made 600, or more, analyses of 210 different sands used in glass making in this country and Europe, and their greatest difference (neglecting H_2O) in the silica content of dry sand is 11.2%. The highest was 99.71 silica, and the lowest 88.51, but the factory using the low grade of sand was producing from it glass of the highest quality, and it was beyond argument with them that this sand was less than 98% pure. In the same factory, about a year later, there occurred a change in management, and the first step taken by the new officials was to change the sand. A pure sand from the Fox River district, analyzing 98.89% Silica, was substituted, but the same results were noted as far as quality and quantity of product were concerned. There was a difference, however, in the chemical and physical properties, and, contrary to the usual belief, the 88.51 sand produced a glass far superior in physical properties to that made by the purest sand, and gave the following values:

SiO_2	88.51
Fe_2O_3	.31
Al_2O_3	7.26
TiO_2	.02
$CaCO_3$	1.07
$MgCO_3$	.43
Organic Matter	.86
Water at 100C	.37
Water at 300C	1.01
Undetermined	.16
	100.00

It will be noted that the alumina was high, and that more moisture was driven off between 100 and 300 than

before 100. Also previous to heating, this sand exhibited some plastic properties, indicating that the loam or clay in it was in the hydrated condition.

The glass analysis gave the following values:

SiO_2	70.51
Al_2O_3	5.98
CaO	9.57
MgO	.81
Na_2O	12.87
Titanium	Trace
Fe_2O_3	.23
	99.97

The 98% Sand gave the following values:

SiO_2	98.89
$CaCO_3$	.18
Fe_2O_3 } Al_2O_3 }	.68
Organic Matter	.04
Water at 100C	.12
Water at 300C	.02
Undetermined	.08
	100.00

The glass produced from the 98% sand gave the following values:

SiO_2	72.01
CaO	12.48
Na_2O	13.21
Alumina & Iron	1.81
MgO	.41
	99.92

The batch formulae for these two glasses were as follows:

No. 1.	
Sand	1000
Lime Stone	230
Salt Cake	365
Carbon	20
No. 2.	
Sand	1000
Lime Stone	330
Salt Cake	390
Carbon	20

When No. 1 sand was first used at this factory, much trouble was experienced with small stones and cords,

which were attributed to the lime, and as a consequence it was reduced until the stones ceased. Believing that when the lime was materially changed it called for a change in the soda or salt cake, this was also reduced, but no one could give any reason for either. However, it occurred that these changes were such as to place the alumina content as a substitute for lime.

This glass showed an increased resistance to tension of 8.3%; for modulus of rupture there was an increase of 21.1% over that of No. 2; however, it was somewhat more susceptible to changes in temperature, and showed considerable higher viscosity at given temperatures, but contrary to expectation, showed little or no lamination and annealed easily at a temperature of 500 C to 200 C in 15 minutes for sheets $\frac{1}{8}$ inch thick, so that no strain could be detected. It was of high luster and had remarkable power to resist alkalies,—acids attacking it to a greater extent, but not as much as No. 2 by several per cent.

One large manufacturing concern was accustomed to washing a certain crushed rock, it costing them from 11 to 16 cents per ton for such work, and it took a great deal of argument to convince them that it was money thrown away. It was discontinued, however, and they made as good, if not better, glass than before, and certainly reduced the factory breakage.

There is also a great difference of opinion as to the size of sand. Some will not use a sand which will not pass a 30 sieve, and others do not want over 10% to remain on a 30 sieve, the remainder not to pass a 40. Again some want 20% through a 30 and the balance through a 40, but none through 60. Others again disregard size completely, but all stoutly maintain that their idea as to size is correct. So far as I have been able to discover, it makes little or no difference what the size is, excepting perhaps if too fine some is lost by being carried away by draft. Of course it is obvious that the less iron in it the better, and for optical purposes it should be free from alumina.

There is usually more injury sustained by allowing foreign matter to become mixed with the sand while in transit or in the storage bins, than by anything that is native to it. As an example, one concern making colored glass could not account for loss of color in their pots until careful investigation revealed the fact that the last car of sand was shipped loose in a car that had previously been loaded with coke; this had not been thoroughly cleaned out, and it acted as a reducing agent.

The amount of sand is usually weighed very carefully, but the amount of water which it carries is seldom, if ever, considered.

LIME

Perhaps the greatest trouble carrier in the list of ingredients is the limestone or lime. This is used in the form of crushed stone of various sizes, air and water slacked, and also sometimes as oxide. In making glass in tank furnaces, the ground stone is mostly used. The size required depends upon the opinion of the individual, as with the sand.

While some of the troubles attributed to the lime are real ones, there are many instances where they are imaginary. Usually it is supposed that a limestone must be as free from magnesia as possible, not to contain over 2% of the carbonate, and should have 96% to 98% calcium carbonate. Until recently I believed that in excess of 4% it was injurious and would produce stones, but I found a plant turning out fine glass with 6% to 9% magnesium carbonate, and using a limestone which would yield but 46½% of calcium oxide, and carried as high as 3.4% of organic matter. This glass was of excellent quality, having an especially brilliant surface and handled well, excepting that it was inclined to be too fluid at working temperatures. Modulus of rupture was about 25% higher with this glass than with a normal window glass.

The fact that certain manufacturers and chemists have decried magnesia, and some have even stipulated in their contracts the limits of magnesia values, naturally led one to believe that magnesia was a serious evil to be avoided, but investigation shows that proper furnace regulation mitigates the evil effects of reasonable quantities of this material; however, I doubt if greater quantities than 6% in the lime would be permissible.

One of the greatest evils to be found in lime is its variability in quantity of available calcium oxide, and the prevalence of objectionable foreign matter, as fossil remains or phosphates, sulphates, and what is termed "ganister", a hard insoluable, refractory silicate of magnesium, lime and alumina, which will invariably produce a small white stone. Calcium, sulphate and phosphate, particularly the latter, will produce a stone under certain conditions of furnace operation, and an opal cast if in too large quantities.

Lime gives to glass, when added in proper quantities, those properties which best adapt it for commercial use, viz., stability or permanency, hardness, viscosity and tenacity, and facilitates the melting and refining of the metal and does not easily devitrify; however, it greatly reduces the crushing strength when existing in quantities greater than 12.95%. When existing in proper proportions with the soda to make 6 silica equivalents to one each of lime and soda and properly melted, it gives the highest tensile strength to any of the elements.

To increase the lime so that the glass will contain more than 12.83% calcium oxide, will tend to make the glass hard, brittle and more difficult to fuse into a perfect glass. Tenacity and hardness increase up to the 13.2% CaO, after which there is quite a rapid decrease in these properties.

SODA.

To here attempt to give a record of all of the experiments made to determine what properties sodium sul-

phate (salt cake), sodium carbonate (soda ash), sodium hydroxide (caustic soda), or the allied potassium compounds give to glass, would be impractical, if possible, and many of the results too confusing to be of much interest; therefore we will only consider the most important ones.

One-hundred-four samples were made in which the above alkalies were used, but I will only give the results that will show the action of these different alkalies generally, regarding which I wish to mention particularly the rather unusual properties of sodium sulphate.

Glasses were melted and an endeavor made to obtain them with the alkali content existing in the percentage of 12, 13, 14, 15 and 16, which we will number according to the desired alkali. Also melts were made using carbonate sulphate and hydroxide of soda, which we will designate under their respective heads. Only two samples of hydroxide were made, as this was of no practical importance and not worth while.

Samples of about 20 lbs. were melted, the material being charged into the pot all at one time, and all melts made at 1525° C. or as near this temperature as possible. The pots were "stood off" and "planed" in the usual practical manner.

The batch formula was so proportioned as to keep the relation between lime, silica, alumina and magnesia as near as possible, they not varying more than about 1.2%, excepting with alumina which, in a few instances, gave as greatest difference 1.42% and occurred when using the hydroxide, and .54% in other samples.

Solubility tests were made by powdering 10 gms. of the sample and allowing it to stand for 48 hours in 100 cc. of distilled water (previously boiled to remove the carbon dioxide) and titrated with centi-normal acid solution, using phenol phthalein as an indicator. The results are given in milligrams. The figures given are average results of two or more trials.

Soda Ash:

Na_2O	12%	13%	14%	15%	16%
Tenacity	12,870	11,400	10,050	7,200	4,150
Crushing	68,900	90,100	91,900	87,600	76,540
Modulus of rupture	4,610	4,810	5,180	4,510	3,890
Solubility	.051	.027	.031	.049	.077
Salt Cake:					
Tenacity	13,200	12,900	10,800	7,300	4,150
Crushing	76,400	93,700	90,200	89,400	68,700
Modulus of rupture	4,800	5,210	5,340	4,870	3,620
Solubility	.003	.003	.007	.014	.053
Caustic Soda:					
Tenacity	11,450	10,420			
Crushing	71,250	64,375			
Modulus of rupture	3,710	2,190			
Solubility	.037	.051			

It will be found that glass made with salt cake, the furnace conditions being the same, is harder, has a higher softening point, greater strength, and is less viscous at 845° C. than that containing soda ash, analysis showing that their composition is practically the same. Also the metal of salt cake has the property of retaining any impression made in or upon it in the form of a cord or wave to a much greater degree than does soda ash, and it requires a temperature in excess of 955 deg. C. to eliminate these defects or to cause the chilled surface of the glass to again amalgamate with the main body, while that of soda ash will readily amalgamate at 900 deg. C. Or, to be more specific, if a pot of glass of salt cake has been allowed to stand open, subject to free radiation and atmospheric influences for a period of two minutes, and a cold iron is drawn across it within the first thirty seconds, there will be found to exist in any article made from the

glass gathered or drawn from that pot, a cord or wave. If this operation be repeated with soda ash glass, it will be found that it has had but little effect. This can be better demonstrated if the glass is drawn directly from the surface in cylinder form, similar to the method of the American Window Glass machines.

What has been the cause of this peculiar retentive property, is not thoroughly understood, but as near as I have been able to determine, it is due to an oxidizing effect, owing to the exposure of the surface to the atmosphere, and the sudden chill has caused an arrangement of the cell-molecule masses at a temperature below that at which it will undergo any change of composition. I believe it is primarily due to there being a layer of superoxidized metal at the surface, and the higher oxygen gives it the property of being more susceptible to any mechanical changes.

I have devoted considerable time to this question, as it is a subject of great moment to the window glass manufacturers, particularly those using the sheet or cylinder drawing machine. I discovered this peculiar condition while acting as Chief Engineer of the American Window Glass Company's experimental department, during a search for the cause of the enormous breakage which occurred at that time, and there appears to be no doubt as to the fact that the salt cake was responsible, not only for many of the cords, strings, etc., but was also accountable for much of the breakage taking place during the early days of machine operation, but I believe, and strongly advocated at the time, that a great percentage of this was due, not to the salt cake being present, but to a poor or improperly melted metal. Subsequent experiments and practice have, in a measure, confirmed this, but I must confess that just what was the cause, and where to find a reasonable explanation of this peculiar phenomena from a scientific standpoint, I am as yet unable to answer with certainty.

CLARIFIERS, DECOLORIZERS, ETC.

Regarding these materials, there is not much of importance to say from a physical standpoint, other than color.

Arsenic, which is used as a clarifier, does increase the crushing strength somewhat, but it is seldom found in the finished metal in sufficient quantity to be noticeable, and the same is true of manganese.

Cryolite, which is used sometimes as a clarifier, is of but little value, and is somewhat detrimental to the furnace or pots, owing to the liberation of fluorine. It would be of some value, could it be used in sufficient quantities to introduce enough alumina to be of importance, but this cannot be done without producing stones, or opal glass.

One frequently hears the remark that a chemist or scientist is of no use in a glass factory. This, no doubt, in a measure is true, for it is seldom, if ever, that a chemist or scientist will be able to find a manufacturer or owner, who would for a moment think of wasting time or money in the consideration or adoption of the suggestions of such individuals, at least not until they are confronted with a situation that legend, sorcery, prejudice and guess work can not account for or overcome.

In addition to the composition and ingredients, consideration must also be given to the fact that melting conditions have a great influence on the physical properties of glass, and the following will give some idea as to the extent. Four melts were made from the same batch, under the same conditions, and all, when finished, had the same general appearance as to lamina, and were practically free from blisters or stones. Test specimens were cut from each of these melts and tested for modulus of rupture, softening point, tenacity, crushing and degree of solubility, as per the following results:

Quantities of 50 lbs. of batch were used and melted in open pots, the batch formula being: Sand 100, limestone 34, salt cake 40 and carbon 1. This produced a glass having a composition of:

SiO_2	73.
CaO	12.75
Na_2O	13.2
Iron & Alumina	1.04
	99.99

The same method of melting was followed in all cases, the pot being brought to the required temperature and 30 lbs. of batch introduced, with subsequent lots of 15 and 10 lbs. The desired temperature was maintained for a period of 6 hours, after which the temperature was gradually reduced to 1100 C. The samples were made in the form of rods, as near one-half inch in diameter as possible, and cut in lengths of 20 inches. These were tested for modulus of rupture by supporting same on two knife edges 18 inches apart, the load being applied by means of a lever arrangement at the center between the supports. The deflection was recorded by movement of the long arm lever which carried a pen, the same being held in contact with the paper by an electro-magnet, which was energized by battery current, in the circuit of which was the rod being tested, and on which a strip of tin foil was fastened by means of shellac. When rupture occurred the circuit was broken, and the pen released by means of a spring. Weight was applied by running mercury in a cup on the lever arm, this being controlled in the same manner.

SAMPLE NO. 1.

	Pot Temperature.
First charge	1590 deg. C
Second charge	1570
Third charge	1560
End of 3 hours	1590
End of 4 hours	1600
End of 5 hours	1575
End of 6 hours	1550
End of 8 hours	1250
End of 9 hours	1100

Glass was clear and free from bubbles. Samples gathered at 1100 not annealed. Modulus of rupture, average for three trials, 5203 pounds per square inch; greatest difference 120.6 lbs. Deflection—.473—.389—.451. The pieces were upset at ends and pulled, three samples being used, indicating an average tensile strength of 11,940 lbs. per square inch; greatest difference 438.4. Pieces of the same rods, 1 inch long, were faced square on the ends and were used for crushing. Average for three trials, 91,300 lbs. per square inch; greatest difference 1248.5 lbs.

SAMPLE NO. 2.

	Pot Temperature.
First Charge	1450 deg. C
Second Charge	1400
Third Charge	1500
End of 3 hours	1525
End of 4 hours	1475
End of 5 hours	1450
End of 6 hours	1475
End of 7 hours	1210
End of 8 hours	1100

Glass was clear and free from bubbles, but somewhat darker in color than No. 1. Sample gathered at 1100° and the metal appeared tacky, and did not have the viscosity of No. 1; sample not annealed. Polarized light indicated some lamina. Modulus of rupture, average, 4720 lbs. per square inch; greatest difference 371. Deflection—.300—.321—.222. Tensile strength, average, 9399 lbs. per square inch; greatest difference 462 lbs. Crushing strength, average, 88,550 lbs. per square inch; greatest difference 7650 lbs.

SAMPLE NO. 3.

	Pot Temperature.
First Charge	1250 deg. C
Second Charge	1350
Third Charge	1400
End of 3 hours	1450
End of 4 hours	1450
End of 5 hours	1425
End of 6 hours	1450
End of 7 hours	1275
End of 8 hours	1100

The glass was free from undecomposed material but showed a few bubbles. Sample was gathered as before and proved to be very unsatisfactory for working. It was ropey, and showed that there was lack of homogeneity. The color was somewhat darker than No. 2, and when examined in polarized light it showed considerable lamination. Sample was not annealed.

Modulus of rupture, average, 3160 lbs. per square inch; greatest difference 417 lbs. Deflection—.108—.217—.214. Tensile strength, average, 8765 lbs. per square inch; greatest difference 481 lbs. Crushing strength, average 78970 lbs. per square inch; greatest difference 7840 lbs.

It will be seen from the above that the melting of glass plays a very important part in producing an article which meets all the requirements necessary to make a first class product. Much more might be said, but this will suffice to give an idea as to what influence temperature has upon the ultimate properties of the metal.

What the glass industry needs and must have before it can become much more than a school of conjecture, is a Wedgewood or a Schott, assisted by a Society of Research, which shall have a backing and be subsidized by the government, or by every manufacturer in the business.

A more extensive field for investigation can not be found, nor is there one which embraces material so widely distributed in nature, or which calls for more exacting and positive conditions to produce definite results with as intricate compounds. It is my opinion that in making a piece of glass there are involved many of the highest physical and chemical laws, if not some which we know little or nothing of at the present time.

Let us hope, therefore, that the glass business may soon see the termination of its antiquated modes of procedure, and be put on the same plane with other modern industries, which I feel assured can be greatly facilitated

by departing from the present predominant "guess work" principles, and introducing co-operation in the ranks of control.

DISCUSSION.

Mr. Orton: Mr. Frink has stated that with impure sand supplies they had nevertheless gotten very good results. I take it that he means in this case that the impurity is to be attributed to alumina and to silicates, such as feldspar and mica, but not to iron-bearing minerals.

Mr. Frink: That is correct and in my estimation a sand that carries with it from six to eight and I might say even ten per cent of alumina is still desirable, provided it is free from iron.

Prof. Orton: Freedom from iron is what you want, then in a glass sand?

Mr. Frink: Yes, freedom from iron is everything so far as color is concerned. However, there is another more troublesome impurity in sand, namely flint or "ganister". When we get that, with what sometimes comes in the lime, and with alumina, we are apt to run into a bunch of trouble. I would say we are using a very nice sand, but every little while we will get a car load from the pit where there is a stratum of pebbles running through the rock which are like flint. They put the sand through a No. 10 sieve which makes the masses of flint of such size as to be extremely difficult to melt and when we get some of that pebble we get stony glass and cords.

Prof. Orton: Does the alumina effect the melting point?

Mr. Frink: Yes it does, but to what extent I cannot say. It affects it providing it replaces lime and also if it replaces the soda, raising the melting point if it replaces soda and probably lowering it if it replaces lime, but the substitution of alumina for either one of these constituents brings it into such a variable condition that I cannot give definite information. I have such a mass of data that

I have not been able to compile it sufficiently to say whether there is a correlation between alumina replacing lime or soda.

Prof. Orton: I might say that I had a very short investigation made some years ago, by one of my students. He took the droppings from the roof of a kiln which had been used repeatedly for salt glazing operations and analyzed them. He found a great deal of alumina but no lime; it was a clear glass with alumina taking the place of lime. Then he made up some mixtures of this sort and fused them in one of our experimental kilns and got very good glasses without using any lime; it was apparently as good glass as the common lime-soda glasses except the amount of iron was higher and hence the color was bad. We did not try to carefully study the properties of the glasses but so far as the eye went, they were as good as any, or would have been if iron-free ingredients had been used.

Mr. Frink: I have taken droppings from the cap of the furnaces and we have sometimes got perfectly clear droppings. Our caps are made of silica brick and upon analyzing the droppings we found they ran 79 to 96 silica, the remainder being lime and soda, with little or no alumina. I do not understand this; you take those ingredients in the same proportion and try to fuse them in a crucible or a pot to a clear glass and you can't get a heat sufficient to fuse without an oxy-hydrogen blast.

Prof. Orton: I think the Society owes a great deal to Mr. Frink for the paper he has presented. It is the first time a paper has been presented on the subject of glass technology and since glass manufacture is one of the three great branches of silicate manufacture, our literature ought to pay more attention to it. We have devoted ourselves almost exclusively to the clay industries and have neglected the cement and glass industries. We have had a few papers upon cements, but only two on glasses heretofore. I welcome this contribution very much on that account. The data contained in this paper is of great quan-

tity and great value, and it comes from sources to which we have not had access before, viz., the laboratories of the largest glass manufacturing organizations in the country.

NOTES ON THE TESTING OF ENAMELED SHEET STEEL WARES.

BY

EDWARD ORTON, JR, Columbus, Ohio.

The lack of standard methods of measuring the quality of this class of goods is beginning to be keenly felt, as the industry is growing with great rapidity and vast quantities of the ware are in use. The writer doesn't know of any method of test having gained any wide acceptance, and in fact only knows of one definite standard having been proposed. This is the test proposed by Mr. C. N. Hooper of Dubuque, Iowa, who is actively interested in the enameled iron industry and has some business as an expert enameller and technical adviser to enameled iron manufacturers.

THE HOOPER METHOD.

The Hooper test is a solubility test, and the method was made public in 1906 or possibly earlier,—at least, a circular letter was issued to interested persons in 1906 giving the modes of testing and results on a number of samples. Further bulletins issued in 1908 state that the solubility test has been supported by the addition of a physical test for chipping and peeling, and also observations on the perfection of the coating with reference to impermeability, or freedom from pin holes, or other defects making attack on the metal possible. The nature of the chipping and peeling test is not stated in the most recent bulletins received by the writer but it is evidently either an impact or bending test of some sort or a sudden heating and cooling test. The perfection of the coat is apparently judged by a mere inspection of its appearance.

The method of making the Hooper solubility test, judging from such statements as are made in the Hooper circulars, is believed to be made as follows:

Hooper Solubility Test. Obtain one dozen pieces of the ware to be tested. Mix chemically pure acetic acid and distilled water in proportions of 10 of acid to 90 of water. Take 500 cc. of this solution, pour into the receptacle and boil it until the liquid has all evaporated. Take off the hot dish with a pair of tongs, cool in water, and clean it with sapolio or sand under a stream of running water, finally drying it. Examine the coating to see if the glaze has suffered any damage. The impairment or loss of the gloss is easily seen in white enamels, but in gray colored ones, it can be felt before it can be seen. The piece must be perfectly dry to enable the sense of feeling to detect the first faint roughening of the surface of the enamel.

If the 10% solution has had no effect, prepare a solution consisting of 20 per cent acetic acid and 80% water, and repeat the trial on a fresh piece of ware in the same way, increase the strength of the acid in 10% steps until pure acid is used, if necessary. The ware is graded in per cents according to the point at which its surface is attacked. These wares are classified as 15-20%, 25-30%, etc., in the reports sent out by Mr. Hooper.

The system described above is of course exceedingly simple, but the statements made concerning it in various circular letters disclose several interesting facts:

1st. There seems in most cases to be no connection between the real ability of the wares on the market to withstand this acid test, and the claims for the acid proof quality on the part of the makers. In the tests published by Mr. Hooper, in which the name, brand, and trade-mark of wares are clearly given, he finds resisting power to the acid as low as 10% or even to 2 or 3%, for wares which are claimed confidently to be *proof against all fruit acids.* One manufacturer advertised on his ware "It will withstand the most severe acid and heat test," but it cut as

readily with a 1% or 2% solution of acetic acid as with 10%, and the enamel was so soft that it melted over an ordinary gas flame.

2d. The wares range in quality from 10% to 100%, one ware being found which could not be attacked by boiling acetic acid, and a number stood from 50 to 80% solutions. The large majority, however, failed to reach the 50% grade, being found in the 15-20 or 25-30 grades. These wares as a rule were the most flamboyant in their claims of excellence.

3d. There seems little if any very close connection between the resistance to solutions of acetic acid, and the resisting power to blows or sudden changes of temperature, or the quality of the surface. On summarizing the July 11th, 1908 bulletin, there were 22 samples tested, of which the properties may be tabulated as follows:

Number of Samples	Present acid required to attack surface of enamel	Covering quality of surface	Resistance to sudden changes of temperature
17	10% or below	10 bad 5 fair 2 good	10 bad 2 fair 5 good
1	20%	bad	good
1	40%	bad	bad
1	50—60%	good	bad
1	60%	good	bad
1	80%	good	good

The difficulty of correlating these properties will be at once apparent.

Neither criticism nor compliment can be extended to the tests used for resistance to sudden changes of temperature, or for covering quality, since neither mode of

estimation is explained in the data furnished the writer. In regard to the acetic acid test, the method proposed has some attractive features. The determination of the concentration of the acid required to attack the enamel seems good to the writer. But, the method suggested of using flint or sapolio to scour the surface after the acid treatment seems to the writer unduly severe and liable in the hands of some operators to lead to destruction of the gloss of the surface from this cause alone.

THE AUTOMOBILE TAG TEST IN OHIO.

In May, 1908, the Secretary of State of Ohio, Hon. Carmi A. Thompson, being required under the new Ohio Automobile Law to purchase many thousands of tags of good quality for automobiles, and being desirous of obtaining a thoroughly good article, commissioned the writer to compare the qualities of 3 different tags which seemed suitable for the purpose. A considerable number of tags had been rejected on various grounds, but of the three surviving competitors, all were of so-called enameled iron. The names of the manufacturers were not given me until after the work was reported, so the samples were marked Nos. 1, 2, 3. A description follows:

The Samples

Sample No. 1. This was a *light* blue tag, 8 inches long by 5 inches wide, with white letters, bearing the figures 8110.

Sample No 2. This was a *very bright* blue tag, 11½ inches long by 5½ inches wide, bearing the number 1235 H, in white letters.

Sample No. 3. This was a street sign, *of bright blue* color, bearing the name OHIO AVE. in white letters. The dimensions were 14 inches long by 4 inches wide.

These samples will be referred to hereafter by number only.

THE COMPARATIVE TESTS.

These tags consisted of pieces of sheet steel of approximately equal thickness, which had been covered with so-called porcelain enamels in two colors, by which the distinguishing numerals or letters appear in one color and the ground in a different color. It did not appear that there was very much importance attaching to the quality of the steel employed, as this steel is protected from the weather and therefore merely acts as the framework or skeleton of the tag. Any steel that might be used would surely have sufficient strength and elasticity to stand far more abuse than any enamel which could be put upon it. The only points about the metal which need consideration, are the thickness of the sheets employed. The character of the enamels used in covering the metal is the real subject of inquiry, for if it fails, the metal itself would be worthless.

These enamels were studied and tested on the following different lines:

1st. Appearance, workmanship and luster.

2nd. Solubility of the enamels in water.

3rd. Solubility of the enamels in dilute acid.

4th. Ability of the enamels to resist acid gases or vapors.

5th. Ability of the enamels to withstand flexure or bending, without cracking.

6th. Ability of the enamels to withstand impacts or blows without shattering.

These various comparisons are based upon artistic, technical, chemical and physical considerations.

Appearance, workmanship and luster.

The conclusions reached under this heading are *purely matters of opinion* or judgment. None of them admit of measurement.

The Coats. The entire surface of each sample is covered with a very thin gray semi-transparent ground coat. On the front side of each is laid a much thicker coat of

opaque white. On top of this is a third coat, covering the bulk of the surface, but not covering certain areas in the shape of letters or figures. This third coat is blue and of about one-half the thickness of the second or white coat. The white figures, therefore, consist of 2 coats and the blue ground surrounding them consists of three coats. On the back side, samples No. 1 and No. 2 have thin white coats on top of the gray ground coat. No. 3 has the gray ground coat only.

Thickness of Coats. The ground coat of each appears to be about the same. In all it is very thin. The white coat is thickest in sample No. 2, next in No. 3, and thinnest in No. 1. The blue coat is thickest in No. 3 and about alike in No. 2 and No. 1.

Color.

The White Enamels. The white of No. 2 is the finest, that of No. 1 next and No. 3 last. The difference is chiefly in the fineness of the grinding of the enamels, and in the neatness with which they are handled and consequent freedom from specks No. 1 has the evenest color and fewest specks, but it is not quite so pure a white as No. 2. The latter has more specks and coarser ones, but produces the strongest and most brilliant contrast with the blue ground in spite of its defects. No. 3 is distinctly inferior in whiteness and in the quantity of specks.

The Blue Enamels. The Blue Coat of No. 2 is the most brilliant blue. No. 3 is a close second as to color, but it is not so well matured an enamel, as it is full of bubbles which weaken the color somewhat. No. 1 is a much paler "washed-out" blue. It looks as if tin oxide had been used extensively to make the blue opaque, at the expense of the brilliance of the color.

Luster or Brilliance of Finish. No. 1 has the most perfect finish. No. 2 next, and No. 3 last. No. 1 has a softer, smoother, more mirror-like surface, on which the defects of the metal show through less.

No. 2 has a more glassy, brighter surface, but it is not so nearly plane, and shows the pits and scratches of the metal underneath, or else is pitted and scratched itself in its application. No. 3 is less glassy and less brilliant than either No. 1 and No. 2. It is more matte or dull in appearance.

Workmanship. No. 1 is slightly the best. No. 2 a very close second. No. 1 excels in neatness and general appearance and is of a very excellent quality in this respect. No. 2 is but little behind it. No. 3 is distinctly inferior to the others.

Summary:

	No. 1.	*No. 2.*	*No. 3.*
Coats.	3 on front. 3 on back.	3 on front. 2 on back.	3 on front. 1 on back.
Thickness of coats.	White, thinnest. Blue, equal. Ground coat, equal.	Thickest. Equal. Equal.	Medium. Thickest. Equal.
Color. White Blue	Second place. Third place.	First place. First place.	Third place. Second place.
Luster. Workmanship.	Most perfect. Finest.	Second place. Second place.	Third place. Third place.
General grades.	Best on everything except color.	A little inferior to No. 1, except on color where it is easily best.	Poorest.

Solubility in Water.

This test was designed to give in a short treatment, some idea of the relative ability of the enamels to withstand the influences of water and weather during a long period of time. Of course the agency employed was much more severe than any natural agency would be, but it was applied for a few hours instead of many years. As all were subjected to the same treatment, it was equally fair for all.

The treatment consisted in boiling pieces of the tags in pure distilled water continuously for 8 hours. The

surfaces were cleaned before putting into the water to remove all grease. The following is the data of this test:

Solubility in Water Test.

	No. 1.	*No. 2.*	*No. 3.*
Size of piece of tag treated.	1⅝"x2⅝" 4.275 sq. in.	2½"x3½" 8.40 sq. in.	3¼"x4" 13 sq. in.
Percentage weight lost by solution.	0.056%	0.037%	0.075%
Appearance after test.	Luster, dulled. Blue more affected than white. Color, dull blue.	Luster dulled. White and blue equally affected. Color still fairly bright blue.	Luster gone. Blue changed to blackish purple, white to yellow.
General results	Medium affected.	Least affected.	Most affected.

The results of the water treatment are very clear and unmistakable. Sample No. 2 has much the best of it, both as to actual amount dissolved and damage to surface and color. No. 1 follows as a fairly good second, and No. 3 makes a poor third, being in a much lower class than the others.

Solubility in Weak Acids.

Since automobile tags are likely to get more or less sulphurous or sulphuric acid from the exhaust gases of the automobile engines, and in electric machines by leakage from the storage batteries and in recharging, when acid fumes are always given off, and also to determine which of the enamels is the most durable and fixed compound and least likely to break down from any chemical cause, it was decided to boil the samples in very dilute sulphuric acid for 15 minutes. Accordingly a solution of sulphuric acid was prepared by measuring out 1 part of the chemically pure acid and 99 parts of water. This was heated to boiling, and the pieces immersed and kept there for 15 minutes.

Before immersion, the edges where the bare iron was exposed were covered with two or three coats of shellac varnish to keep the acid away from the iron. This was only partly successful, as it came off before the 15 minutes was up. It undoubtedly hindered the acid from attacking the iron for a while.

The following are the results:

Solubility in Dilute Sulphuric Acid.

	Sample 1.	*Sample 2.*	*Sample 3.*
Size of test pieces.	1¾ inches by 2⅝ inches.	2⅝ inches by 2⅝ inches.	1¾ inches by 2¾ inches.
	4.58 sq. in.	6.55sq.in.	4.82 sq. in.
Percentage weight lost.	0.72%	1.06%	4.85%
Condition of the enamel after test.	Surface dull. No luster. Blue, very pale, and gray looking. Contrast between blue and white portions weak.	Surface dull. No luster. Blue still bright and strong and contrast between blue and white portions good.	Surface very dull and rough. Pitted. Back nearly bare of enamel. Blue faded almost to white. Very little contrast left.
Results.	Considerably affected.	Least affected.	Very badly affected.

These results of the acid boiling test are nearly as clean and unmistakable as the results of the water boiling test. No. 2 enamel has the best of it, so far as appearance goes. The percentage loss is slightly against it, but the area exposed was much larger and the amount of free iron which the acid could attack was greater. This, rather than the enamel, is the probable source of the higher loss. As elsewhere No. 3 is far below the others in quality.

Resistance to Acid Vapors.

The reasons for this test are the same as those given in the preceding section. The acid used was hydro-

chloric, since it is much more volatile; sulphuric acid would require a much longer exposure to accomplish equal results.

The procedure used was to expose the pieces for 18 hours in a bell jar, in which a beaker of strong hydrochloric acid was sitting. No heat was used and the pieces were attacked by gases only. After exposure, the tags were washed in distilled water, dried and weighed.

	Sample No. 1	*Sample No. 2*	*Sample No. 3*
Size of test pieces.	1½"x2½" 3.75 sq. inches.	2⅜"x2 13/16" 6.7 sq. inches.	2"x2⅞" 6.75 sq. inches.
Percentage weight lost by washing salts off which had formed by attack of vapors.	0.453%	0.190%	2.62%
Condition of surface after test.	Surface dull. Blue somewhat bleached. Contrast in color much affected.	Surface bright. Blue still brilliant and contrast not visibly affected.	Surface rough and gritty. No glaze finish left. Blue color still strong and contrast still shows up well.
Results.	Considerably affected.	Very little affected.	Very badly affected.

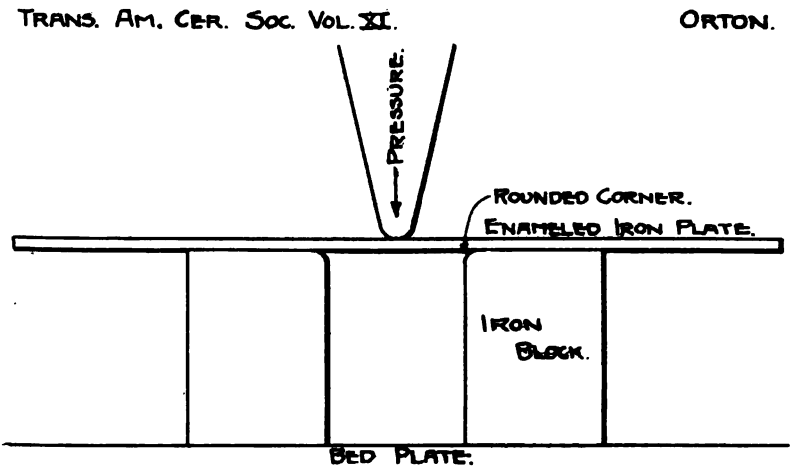
This experiment gives the most striking results of any of the chemical tests made, and confirms both the others in showing sample No. 2 to be the hardest and most resistant enamel of the three to all ordinary chemical attacks.

Bending Tests.

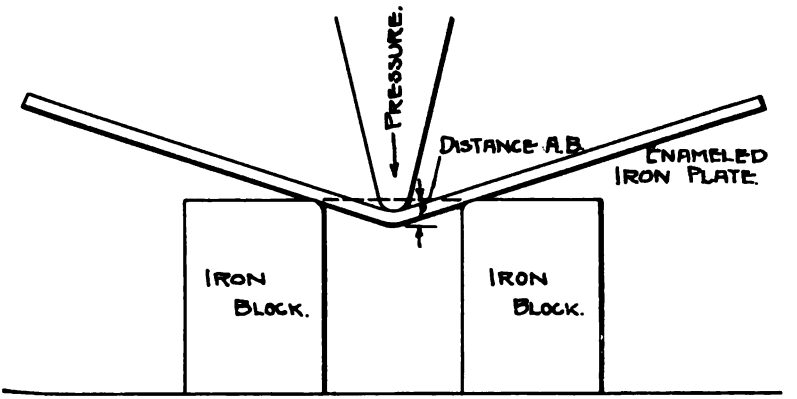
All enamels, being merely glasses, are liable to cracking on flexure, even gentle or moderate flexure. They are

especially so because attached to a metal base and not free to contract or expand of themselves.

To measure their relative elasticity or power to bend without cracking a special apparatus had to be constructed. It consisted of a pair of steel bars, held rigidly



SKETCH OF APPARATUS READY TO APPLY PRESSURE.



SKETCH OF APPARATUS WITH PLATE UNDER LOAD.

DISTANCE A.B. IS THE MEASURED DEFLECTION.

by bolts and washers until they stood 1 inch apart and parallel. The inner edges were rounded so as not to cut the surface of the enamel. The plate to be tested was laid on this frame and a rounded knife-edge was brought down on it, in increments of one-hundredth of an inch at a time. After applying each deflection load, the piece was released and examined under the glass for cracks.

	Sample No. 1	*Sample No. 2*	*Sample No. 3*
Condition after flexure of a. b. = 0.01″	No cracks.	No cracks.	No cracks.
a. b. = 0.02″	Very faint cracks seen under glass.	A number of cracks, but short ones.	Very very slight cracks.
a. b. = 0.03″	Cracked clear across in several places.	Badly cracked clear across. Peeled at one point.	Cracks a little worse, but not clear across piece.
a. b. = 0.05″	Cracked badly. Enamel flaked off a little. Metal shows permanent set of .018 inch.	Badly cracked and chipped. Worst of lot. Permanent set of .025 inch in metal.	Seriously cracked and some chipping. Permanent set of .019 in metal.
a. b. = 0.25″	Smallest permanent set of metal. Narrowest zone of enamel chipped off. Metal clean. Ground coat comes off with the enamel. Does not stick as well as No. 2.	Heaviest permanent set of the lot, because thickest metal used. Large chips of enamel off, wide zone of damage. Ground coat sticks pretty well.	Heavy permanent set of metal. Wide zone of enamel chipped off. Ground coat still sticks better than No. 1 and not so well as No. 2.
Results.	Cracks about same as No. 3, but chips off least of the three. Thinnest metal. Ground coat sticks least.	Cracks earliest and worst and chips worst on heavy bending. Heaviest metal. Ground coat sticks best.	Cracks about same as No. 1, but chips much worse. Ground coat sticks fairly.
	Best results.	Worst results.	Second best.

The results of the Bending Test are not of very great importance. All the enamels stand a slight bend without cracking. All crack at a deflection of .02 inch. Their relative degree of chipping under heavy deflections and the relative adhesion of the ground coats are perhaps more important.

No. 2 shows the worst results. In my opinion it is because the metal is thickest and the enamel is thickest and therefore is more rigid. Its ground coat sticks best of all.

Resistance to Blows.

The probability of damage to automobile tags is greater from this source than from any other physical cause. Flying gravel and stones will hit them; mechanics will try to straighten them or perforate them, etc. To get at their relative resisting power to blows, both heavy and light, the following methods were used:

Page Impact Machine. This machine has an automatically driven hammer, like a miniature pile driver, the hammer part weighing 1 kilogram (2.2 lbs.). The hammer can be lifted and let fall at any height from 1 to 9 centimeters. Hence, the blows can be regulated exactly and each blow made exactly the same in severity.

The results of the Page machine test go to show that sample No. 2 stands impact much the best of the three enamels. No. 3 and No. 1 are more nearly equal though No. 3 has the best of it, so far as can be judged.

The blows given in the Page machine are all light, and reliance was placed on the effect of *long continued pounding* on one spot to test the elasticity of the enamel. This effect is pretty clearly brought out in the following table:

Page Hammer Impact Test.

	After 10 blows.	*After 20 blows.*	*After 40 blows.*	*After 75 blows.*	*After 100 blows.*
Sample No. 1	Slight chipping in one spot.	No increased effect.	Started cracking in another place	.....	.....
Sample No. 1	Crack started in three places.	1 small chip out.	2 chips out. 1 deep one.	Holes widened and deepened.	Holes merged into one big one.
Sample No. 1	Chipped badly on 3rd blow; by 10th blow, the area was nearly bare.	.....	.....	.....	.....
Sample No. 2	No cracks.	No cracks.	No cracks.	No cracks.	No cracks.
	No cracks.	No cracks.	Chipped a little at one point.	Chipping at a new point.	Chipped at 2 points but not badly at either.
Sample No. 3	No cracks.	Minute cracks.	Chipped into quite a hole at one point.	Hole much larger. 2 new ones started.	Scaling off pretty badly.
	Cracked in center of area hammered.	Chipped off a little.	Not much worse.	At 50 blows, the enamel flew off in a big piece 4 or 5 times as large as the area hammered.	

It was thought desirable to also try the effect of a few much heavier blows. These were given by another machine, called the Boehme hammer, which was originally devised for tamping cement into brickette molds uniformly. Blows of four different grades were obtained on this machine, all of them more severe than the heaviest blow the Page machine could give. The tabulated results follow:

Boehme Hammer Test.

	Lightest Blow.	*Medium Light.*	*Medium Heavy.*	*Heaviest Blow.*
Sample 1	Not hurt.	Not hurt.	Not hurt.	Not hurt on enamel face. Rear side cracked.
Sample 1	Not hurt.	Not hurt on top. Crazed on bottom.	Spalled badly clear down to the metal.	.....
Sample 2	Not hurt.	Badly crushed and spalled.	.....	.....
Sample 2	Not hurt.	Badly crushed and spalled.	.....	.....
Sample 3	Not hurt.	Not hurt.	Not hurt.	Not hurt.
Sample 3	Not hurt.	Shattered slightly.	Shattered badly.	.....

The results of this test are somewhat astonishing. No. 2, which stood long continued pounding with practically no effect on the Page machine, here shows itself unable to resist a severe blow at all.

No. 1, which gave way under the Page test very badly in 2 out of 4 tests and failed somewhat in the other two, now stands far ahead of No. 2 and a little better than No. 3.

GENERAL SUMMARY OF THE EVIDENCE.

The condensed results of these tests are:

1st. Sample No. 1 is affected somewhat in all three chemical tests and stands second in this line of comparison.

In physical tests, it stands first in bending and heavy impacts, but fails on long continued light blows.

2nd. Sample No. 2 is affected very little by any of the chemical tests, and shows itself an excellent resistant enamel in this respect.

It stands long continued light blows without much damage but shatters badly on bending or on heavy blows.

3rd. Sample No. 3 is affected very seriously by all the chemical tests, being very much the softest and least durable of the three. It stands bending and heavy blows not so well as No. 1, but better than No. 2. To long continued light pounding it fails.

Conclusion on the Tag Test. A study of the foregoing leads us again to the same conclusions. 1st. Wide differences are found in solubility either in water, or dilute acids, or even acid fumes, between enamels of apparently equal quality. 2d. No correlation can yet be shown between chemical resisting properties and physical strength or beauty of appearance and finish. It seems as if excellence in several directions might be possessed by one and the same piece of enameled metal, but there was no causal relationship between these various kinds of excellence and it is much more likely that any single piece will be deficient in one or more directions.

GENERAL CONSIDERATIONS.

For what kind of properties ought enameled iron to be tested and to what degree or measurable basis of comparison must a piece of enameled ware show these properties.

In the first respect, it is evident that the chemical qualities of an enamel are of different degrees of im-

portance in different wares. For table ware, culinary ware, sanitary and toilet ware, surgical ware, photographic and chemical utensils and all similar purposes, easy solubility is the worst possible fault, both because of the short life of the utensil and because of its unsanitary condition and the impossibility of getting it clean or keeping it clean after it once suffers corrosion or pitting by solution. For street and advertising signs, for automobile tags, for any use in which the ware comes in contact with no hot or acid fluids, or more stronger than the mildly acid waters which fall as rain in our cities, it is evident that solubility in itself is a much less vital consideration.

In the second respect, it is also evident that the possession of physical strength, elasticity, hardness, ability to withstand impact without shattering, power to withstand flexure without cracking or flying off, all of these are also of much greater importance in wares of the utensil class, than in wares of the display or sign class. For, in event of the surface of a ware being defaced by chipping from any cause, the danger from unsanitary conditions, and the liability of breaking down by exposure of the metal underneath, immediately becomes great. Naturally physical defects are objectionable in all classes of goods, but in this class, they are preferable to chemical, for the reasons given, and they are less harmful in wares of the display class than in the utensil class.

In brief, utensils need to be of much higher technical excellence than display goods, because of their exposure to more severe conditions in use and because of the much more serious consequences of their failure.

It has been shown that chemical and physical excellence are not mutually dependent nor are they mutually incompatible. It remains therefore for manufacturers to study their products along both lines and by processes of elimination to weed out those enamels which are found to be of poor quality in one or both respects.

The question of standard methods of test to which wares should be subjected in determining their quality is one which ought not to be subjected to further delay. The question of the standards which wares of any given sort ought to stand when tested by these standard methods ought to be adjusted.

It does not appear that enough work has been done as yet to make it possible to adopt other than very tentative methods and standards. The standards required by the Secretary of State of Ohio for automobile tags in that state were based on the few foregoing tests, for lack of better. They were

1st, 0.05% maximum solubility in distilled water, after 8 hours boiling.

2nd, 1.50% maximum solubility in 1% sulphuric acid solution after 15 minutes boiling.

3rd, 0.50% maximum loss after exposure to HCl vapors for 18 hours and washing off in distilled water.

These very crude and hastily devised standards had the immediate result of taking a $10,000 contract out of the hands of the lowest bidder, for after receiving the award of the work with those restrictions, they promptly declined to meet them or any similar tests and declared their wares were all right, and did not need such outlandish tests to prove that they were. The other bidders who could and did meet this test then got the work.

The writer does not suggest or recommend even the temporary adoption of any of the above terms on this meager evidence. He merely desires to call attention to a situation which urgently needs to be dealt with and which this society is more able to cope with than any other organization in the country, and to point out that physical excellence, as measured by ability to resist moderate blows without peeling or cracking and chemical excellence, as measured by the ability to resist solvents without breaking down must both be required for wares of the utensil class,

while for wares of the sign or display class, chemical excellence is the more important of the two and even that need not be of at all equal degree, to insure a satisfactory product.

DISCUSSION.

Mr. Orton: I wish to say, gentlemen, that these notes are mere scraps of information, and I have not attempted to enter into a discussion of them. If they have any value at all, it will be to draw the attention of other people who have more time to work it out.

Mr. Chormann: Did you make chemical analysis of any of these three enamels?

Mr. Orton: No; we did not.

Mr. Chormann: You mentioned Hooper's tests. I came across his tests as to the comparative durability of different enamels. It seems to me his tests do not give sufficient data for comparison. For instance, he speaks of tests being made with five per cent acetic acid; but you cannot tell whether this strength is constant to the last; whereas if it was known that the strength was maintained constant, and the area exposed to the solution was maintained constant, we would have more valuable results. As it is, we do not know whether the percentage of strength of the solution increases as evaporation proceeds, or whether it decreases.

Mr. Orton: I think that criticism is a very just one.

Mr. Barringer: Mr. President, I want to call attention to a test which Professor Orton did not mention, as applied to enamels for electric heating devices. (Making drawing on board.) This is a test relating to the conductivity of the enamel where it is intended for use as electric insulation. Take a sheet iron pan of convenient size, six or eight inches in diameter, enamel this inner surface at the bottom with the enamel to be tested, then place a resistance coil upon the enameled surface (indicating). The coil is round, in this form (illustrating), and fits inside

the pan, which is circular. Then connect the leads of the coil to, say a 125 volt D. C. circuit. Then make another contact to the bottom of the pan (which is not enameled on the outside), bring down here, connect with a volt-meter, and run it into one side of the circuit with which the coil is connected. The coil is held down with a slab of asbestos board to make good contact with the surface of the enamel. When there is no current on the coil, consequently no heat on the enamel, of course, there is no deflection of the volt-meter. When the current is allowed to flow through the coil and the temperature is raised thereby, we will find that at about, say, 160 to 170 degrees C. we begin to get deflection of the volt-meter, showing leakage through the enamel. The deflection may be 5 or 10 points. These figures are approximate, but will serve to illustrate the experiment. Assume at 170 degrees we get a deflection on the volt-meter of five volts. As the temperature continues to be raised the deflection on the volt-meter becomes greater; so that in the neighborhood of about 500 degree C., the deflection is ninety volts. If you have only 125 volts on the circuit and have ninety volts deflection shown, the enamel is leaking badly, indicating that it is practically worthless as an insulating coating at this temperature. In making an enamel for this purpose it is necessary to make this test and select the enamel having the least deflection at a given temperature.

In testing the various enamels, we have found, by the way, that they all leak so badly at temperatures easily attained in electric heating devices, that we could not use any of them except by fusing across the surface grains of quartz, about the size of rice grains.

After we obtained our enamel surface, we simply spread on the quartz grains and fused them into the enamel. Then the coil is held from the surface of the enamel by these little points of quartz which project above the enameled surface.

It occurred to me that, perhaps, while this test is of minor importance and might only be applicable to those enamels proposed to be used for electrical insulation, a direct bearing might be gotten as between the conductivity and the losses the enamel would show when treated with the various acids. For instance, I imagine that an enamel which is a very poor insulator would show the highest loss when tested with acid. The fact that it is a poor insulator shows that it is a glaze with more or less soluble salts throughout the mass. As bearing on that, we found that an opaque, white glaze or enamel was the very poorest, and the best was blue. It occurred to me that perhaps the small per cent. of cobalt present in the blue enamel had entered into silicate combination rendering the enamel a better insulator than the white glazes where, probably, there are suspended oxides or salts which showed in leakage at comparatively low temperatures. If we could work out a test of this sort it might demonstrate solubility more quickly than by the acid test. I suggest this as showing the possibility of getting data on the different enamels in regard to their value as to solubility.

Mr. Orton: If I make a series of solubility tests by a chemical method and send the results to you, will you make this electrical test on a lot of the same wares and thus get a comparison between the two methods?

Mr. Barringer: Yes; provided there is not a great deal more of the work than I anticipate.

Mr. Frink: There is a company in Germany manufacturing enamel ware which has a test similar to that, and I think I have data of such tests showing the solubility of enamels containing certain oxides. They have two tests to which they submit their ware. One is to place the dish upon a disk in which there is a hole, then drop a weight so that it strikes the plate over the hole. That is an impact test, and they increase the weight until the enamel shows a fracture. Then they have a test something like the electrical test described, only they wrap

the wire around the dish and attach to the metal a bar of iron, and determine the resistance at different temperatures.

They have another solubility test in Europe which perhaps is a more accurate factor; and that is by the vaporization of acetic acid which passes through a tube in which the ware is placed, and then determining the amount dissolved by evaporation of the condensed solution.

Mr. Orton: Do you think that is any better than the easier way?

Mr. Frink: It is more difficult to carry out and besides it always leaves a residue on the ware which must be washed off. It is much more tedious and laborious, but it is accurate, I suppose. They claim it is.

Mr. Orton: I want to say in closing that I hope some of the younger members of the society who are looking for a nice subject to take up for investigation, will sit up and take notice of this topic. It is not a particularly hard one to work out, but it does need persistent and careful work by someone to devise a standard which will meet acceptance over the country. The acceptance of any standard grows slowly, and it is difficult to get the country at large to accept it. There certainly is a need of this right now, and I believe if a critical examination of the existing wares on the market could be made, free from personal bias, that results of value could be brought out. I think it is a good opportunity for some person to make a mark on the enameled iron business of the country.

PYRO-PHYSICAL BEHAVIOR OF FLINT FIRE CLAYS —A CORRECTION.

BY

HARRISON EVERETT ASHLEY, Pittsburg, Pa.

In the paper of the above title by Ross C. Purdy in Vol. X, p. 365, of the *Transactions,* an unfortunate error has been made in the inadvertent use of an incorrect formula. On p. 369, the formula for computing original volume from the cubical fire shrinkage should be $\frac{W-S}{I-F}$ where W is the weight of a brick saturated with water, S is the apparent weight when suspended in water, consequently W—S is the weight of water displaced and equals the volume if grams and cubic centimeters are the units employed; also F is the cubical fire shrinkage exprest as a decimal part.

Column 10 of Table I is then erroneous, also columns 3, 4, 5, 6 and 8 of Table II; as these depend on the formula above. The same errors are repeated in the tables on pp. 373 and 374. As a consequence the "Error in Vol. Determination Due to Incompl. Saturation" shown in the figures on pp. 372 and 377 does not exist; and what is shown is mainly the error due to the employment of an incorrect formula.

The writer having found that such measurements as those made by Prof. Purdy in this investigation give the most accurate information obtainable on the progress of vitrification, takes this occasion to express his appreciation of this particular research, and trusts that Prof. Purdy will present more of such valuable data in this line.

A NOTE ON PUG MILLS.

BY

GEORGE SIMCOE, Northeast, Md.

I find no article in the *Transactions* that gives us any specific data on pug mills, and it is indeed important for there are few potters who have not had trouble with their pug mills. In the electric porcelain industry we are required to have a much better degree of pugging than any other branch of the trade. Permit me to enumerate some of the pugging difficulties:

1. Laminations — spiral, longitudinal and transverse.
2. The dependence upon human agency for uniform feed.
3. The difficulty in adding water to hard clay (pumped hard or dried hard) to bring it to the right temper and yet have it flow through the mill at proper speed.
4. Heating of clay and mill, and clay coming out like sawdust.

To locate and, if possible, correct all or part of these difficulties, was the object of this investigation. The investigation was confined to one body, viz., a very plastic porcelain body. All work done was of a very practical nature, as the following will show:

Cross sections of clay from 1 inch to 3 inches thick were cut from the rolls of clay at various stages from pug mill to bench of jigger (the average per cent of water found to be 21.2%), and carefully worked until the laminations were all brought in evidence. The various shapes taken by these laminations were carefully studied, (See Figs. 1, 2 and 3) and, as you will see, the cause appears obvious, — namely, in the worm or screw propeller, but

FIG. 1

FIG 2.

on placing a plate with three holes in the nose of the pug mill and making three bars instead of one we find the same spiral tendency. That would seem to modify our deductions. However, a careful scrutiny of the lamination itself showed a dry section, or rather, the splitting apart of two dry surfaces that had in only a very slight degree united or welded together. An investigation of the actual condition of the worm showed

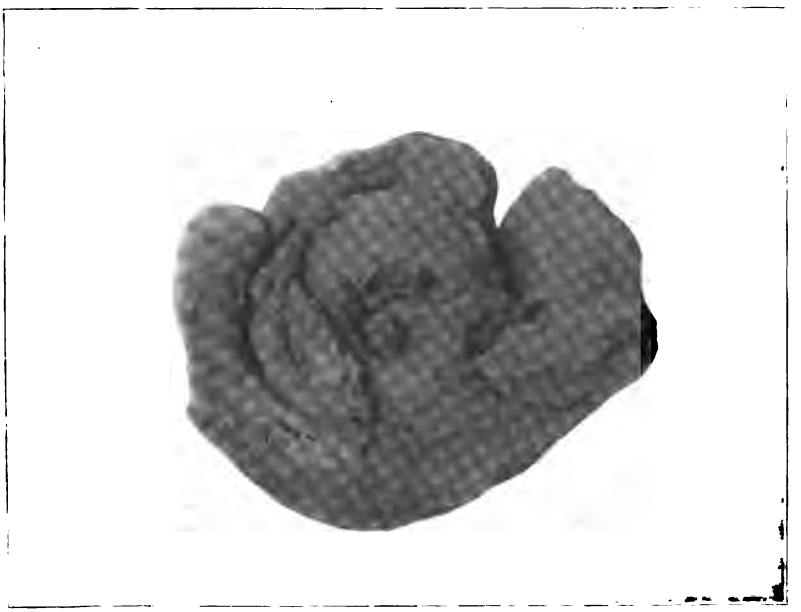


FIG. 3

that the thin film of clay that adheres to it during the process of pugging was dry and of a nature resulting from the rolling and flowing of the other clay over it. This film is kept constant by the dry clay coming off and fresh clay adhering to it. To overcome this difficulty we wet the worm, the result being that we got no flow at all, showing that there is need of a degree of friction between the mass of the clay and that which adheres to the worm.

FIG. 4

FIG. 5

Other cuts were made longitudinally through the bar or roll of clay at various distances from the center. The most pronounced types are shown in the cuts at the center and half way between center and circumference. (See Fig. 4 as illustrating former and Fig. 5 the latter).

We see that in Fig. 4 there is a core at the center and the laminations radiate from it. From these the conclusion was that we had on our hands what the brick maker has for many years fought, with oil, steam, water, etc., —namely, differential flow. I was not able to investigate along this line. A representative of our Company had

FIG. 6

occasion to visit one of the large clay working machinery manufacturers and the point of pug mill laminations was brought up and the statement was made that they had been working on the problem for five years and had not as yet been able to make a machine that would eliminate the laminations. A piston machine was suggested and it was stated that a straight longitudinal crack resulted. It was suggested by them to use softer clay, i. e. pumped soft. We tried this but with little or no improvement.

We use, in making small tubes and bars, an ordinary sausage machine fitted up with nose, spider and mandrel which works fine (See Fig. 6). We were about to build a machine somewhat after this type, when an advertisement in one of our trade magazines showed our ideas were actually on the market. We wrote the manufacturers of this machine requesting that they try out a sample of our clay which we shipped to them direct from presses, packed wet. They very kindly co-operated with us, but results were as before; if anything, worse, because they had evidently pugged the clay over several times until it became brash

FIG. 7

or like sawdust. (See Fig. 7). I then took the matter up with our body maker and found that he was using a large quantity of dry scrap. A reduction in the quantity of dry scrap gave us our clay O. K. As this particular evil was corrected at the hands of the body maker, the work was a success, in that it located the evil and showed means of correction, but we still have the proposition of getting clay not laminated from a body containing large quantities of dry scrap. Is it a problem

for the body maker or the *pug mill* maker? I will not presume to answer this, but some one here may, and it will be mighty valuable information. Because if you make ware you are bound to have scrap and you must use up your scrap in your body, and if you do, under present conditions, when you make a *thick* piece of ware, say 1 inch to 3 inches, if the clay is not wedged, cracks will open up that correspond to the laminations; if the clay is wedged or chummed, better results are gotten, but it is my belief that much of the trouble known as dunting, is traceable to pug mill laminations.

In conclusion a word as to the taper of the nose and distance of mouth of die from the worm. The former is the cause of much trouble, one of which is back flow, due to too much taper. We found that there existed a ratio between the diameter of the barrel of the mill and the diameter of the outlet in the nose. In our large machine, which has an 11 inch barrel, 4 inches is the smallest size bar you can safely make and in the smaller mill the barrel diameter is 5 inches and about a 2 inch bar is safe. When you must decrease the size of bar below the size of safe minimum, have a multiple nose made that will take care of the same total cross section as will work best with the machine.

The distance of outlet from end of worm is quite a point to consider, as back flow will result from the distance being too great and an unsightly corrugated effect on the surface of the roll will occur when the distance is too short. I should say that for making bars larger than 4 inches or 5 inches diameter, 8 inches to 12 inches was safe and satisfactory and that for less than 4 inches, from 8 inches to 5 inches will be equally good.

The vertical type pug mill having a 24 inch barrel and a 6 inch nose may be a very good type for a C. C., P. G. or W. G. body, which is very short, but for a dense porcelain body it certainly can be improved upon.

In Mr. Stull's paper on "Making Front Brick without Repressing," he points out that compression in the nose

is followed by expansion as soon as the clay leaves the outlet. This clay, when dry, develops superficial cracks, tho he does not bring out whether the reduction of taper which eliminated the superficial cracks had any effect on the differential flow. It would be natural to conclude it would.

From the facts brought out by this investigation, I am convinced that many manufacturers have been only too glad to lay the blame for bad ware at the door of the jiggerman and presser, or kiln setter or burner, when in reality the fault was in the preparation of the raw materials.

Therefore, permit me to recommend the practice of taking a number of samples of clay from your pug mills each day, keep a record of same, and as a result, I am sure you will get at the real root of your cracking.

DISCUSSION

Mr. Gorsline: Mr. Simcoe has touched upon the merits of the piston machine, and I think it would be worth while for him to say something more on that subject.

Mr. Simcoe: In reply I will say that I know practically nothing about the piston process. This was only a suggestion made to manufacturers of such machines. They had evidently had experience with them and claimed the result of using them was a longitudinal crack. That is all I know.

Mr. Gorsline: There are certain classes of ware, fireproofing and smaller sizes of conduits, that are made both ways, with the horizontal pug mill and the horizontal piston machine. The people I talked with have been unable to come to any conclusion as to which is the better method.

Mr. Stover: There is a question in connection with this pugging proposition which a little time and experience has worked out, not so important to the horizontal as to the vertical type: that is, the shape or pitch of the knives. We all know that a tear is hard to overcome. We

can press the clay together, but it is likely to get a fracture or tear apart, or redevelop in firing. Our experience has been that the shape and pitch of the knives has a great deal to do with it.

As to the question of adding dry scrap in the pug, it is simply a clay of different temper and it pays to put it back into the blunger. I know in one case parties had to use a kneading machine such as large bread makers use. They had knives put in the bread mixer and mixed the material in that. They thought they got more thorough mixing from kneading than from pugging.

Mr. Simcoe: This clay scrap is not added at the pug mill, but is added to the body in the blunger.

Mr. Stover: And you have got to add it in the right quantity.

Mr. Simcoe: Yes.

Mr. Richardson: Mr. President, it would be well to have that emphasized in the discussion, inasmuch as Mr. Simcoe said he located trouble in that clay scrap, and to have him describe the previous preparation of the clay.

Mr. Simcoe: I will add that.

Mr. Richardson: Is the clay scrap and other clay ground up and washed?

Mr. Simcoe: Mr. Watts had that in charge; but the method of preparation so far as I know was this: the body, consisting of the various materials, was laid out on the floor and a certain proportion of the dried scrap added to it. This was done before it was dumped into the blunger, or the ball mill which was used instead of a blunger; and by this method of using the dried scraps, we got good results. If they increased the proportion of dried scrap it made a very brash clay. And right here it might be well to raise a point in connection with this colloid theory, as to whether or not this drying which takes place in the scrap is carried far enough to destroy the action of the colloids. We dry some ware at a temperature of 120 and sometimes to 130 degrees.

Mr. Stull: I will ask Mr. Simcoe to give us his interpretation of differential flow? I do not understand what he means by it.

Mr. Simcoe: Well, so far as my understanding goes, differential flow is a matter of the speed of the central portion of the clay bar being greater than that of the part that lies close to the die itself.

Mr. Campbell: It was suggested that perhaps we might get away from lamination by the piston method. I will state from my experience, we did not get away from lamination by use of the piston method of making brick.

Mr. Yates: I will inquire if there are any back pressure knives in that pug mill?

Mr. Purdy: What do you mean?

Mr. Yates: Take the pug mill and put these back-pressure knives in and throw the clay back. It lengthens the fiber by that back action. The more you work the clay, the longer the fiber of the clay is and you increase plasticity. If you don't have the back pressure you will get the lamination.

Mr. Purdy: You mean, the knife at a backward angle?

Mr. Yates: Yes, sir.

Mr. Simcoe: In the mill I have in mind,—our regular pug mill,—the worm carries the clay out to the nose, placed at right angles to the feed. That is all I know about back pressure.

Mr. Watts: In this connection, I think I can straighten the matter out a little. In these pug mills we introduced at two different points a straight iron bar across the pug mill in such position that it would not interfere with the passage of the paddles, but in such a way that the flat surface would be exposed to the clay and thus act as a retarder, after the principle suggested by Mr. Yates. The bar itself does not move, but the fact that it has a retarding action tended to assist in overcoming some difficulties we experienced.

Mr. Yates: We suffered greatly with laminations at Shawmut and that was one of the means we adopted in overcoming it. We have three sections with one row of back-pressure knives which holds back the clay, and consequently breaks up the warp.

A METHOD MAKING POSSIBLE THE UTILIZATION OF AN ILLINOIS JOINT CLAY.

BY

A. V. BLEININGER AND F. E. LAYMAN.

A large part of Northern and Central Illinois is covered by the so-called joint clays which are of glacial origin and vary in depth from one to five feet. These clays are weathered to different depths and in this condition they form the basis of a considerable brick industry. They are red-burning surface clays, extremely fine in grain, but as is characteristic of glacial deposits, admixed with mineral detritus of all kinds. In a number of localities, however, they are quite uniform in composition for considerable areas and free from excessive amounts of rock debris, gravel, etc.

In the weathered condition they usually work up quite well into bricks and tiles though they are sometimes liable to check in burning. Some distance below the surface, however, they are apt to show a peculiar behavior in drying, giving rise to characteristic splitting and cracking.

When made into bricks they split through vertically into more or less regular cubes, the same thing being observed when a bank is stripped and the surface is drying out. The loss arising from this peculiarity in attempting to make clay products out of this material is quite considerable, since the checking occurs in the drying as well as in the burning, the latter being due probably to incipient cracks.

A typical deposit of this character is found on the land of Mr. J. W. Stipes, close to the city of Urbana, Ill. This clay is extremely fine grained, red burning, very sticky and plastic but not high in bonding power. Within

a foot of the surface it has been changed by weathering so that it does not show the peculiarity mentioned above to a striking degree but at a somewhat greater depth its true joint structure appears. There are no differences in color noticeable between the weathered and the unweathered portion, both are of about the same yellow. The clay is comparatively free from mineral debris and stands up remarkably well in the kiln. Though at present used for the manufacture of soft-mud bricks and burnt in up-draft kilns, this process does not do the clay justice and does not bring out its best colors, as a down-draft kiln would do. It vitrifies between cones 3 and 4. When burnt at a lower temperature it produces a fine red color.

It has been realized from experience that both weathering and thorough air drying help considerably in overcoming the difficulties encountered in the use of this clay. Hence, by allowing it to freeze through the winter it would become quite workable in the spring. The difficulty is, however, in being sure that all of the clay has been sufficiently weathered, and though the drying loss may be reduced, some loss in burning may still be found to occur. the same thing applying to the air drying.

Considering the benefit derived from air drying, it was proposed to carry this process further and to dry the clay at higher temperatures. For this purpose a sample was taken from that part of the bank, used by the Sheldon Brick Company, that had given the most trouble.

In the preliminary work, small samples of this clay were dried in a laboratory air bath at 100, 200 and 300°C. These were then pulverized, passed through an eight mesh screen, tempered, wedged and pressed into bars, 10″ x ½″ x ½″ in a brass mould. A portion of the undried clay was also wedged and pressed in the same mould. After drying in the air at ordinary temperature the linear shrinkages were determined. It was found that the bar made from the undried clay warped very badly as well as

the bar made from the clay dried at 100°, but that the bars moulded from the clay dried at 200° and 300° showed very little warping.

The linear shrinkages were as follows:

Undried Clay	10.3	Per cent.
Clay dried at 100°	9.7	" "
Clay dried at 200°	7.3	" "
Clay dried at 300°	7.1	" "

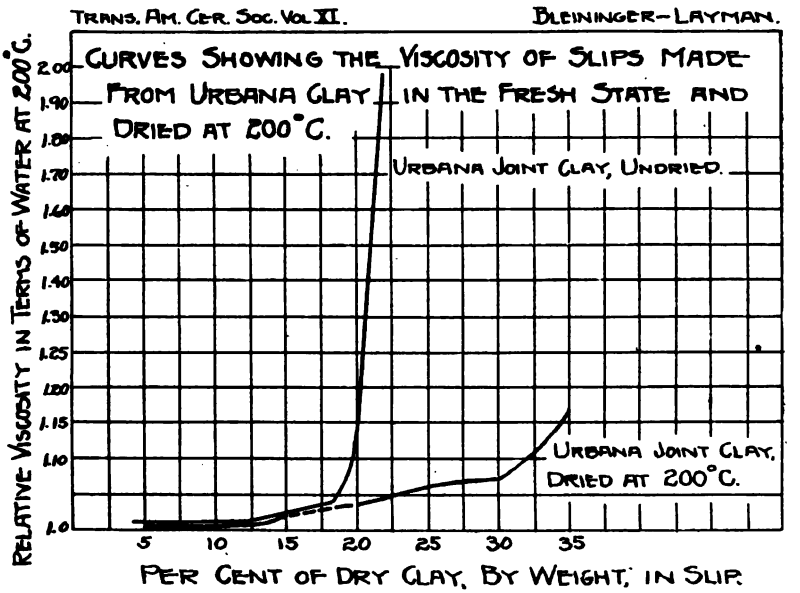
In tempering the dried clay it was observed that the sample dried at 100° still possessed the sticky nature of the undried clay, while the charge dried at 200° had lost to a very large extent this characteristic property. At the same time a certain granular appearance was noticed as well as a slight change in color from yellow to reddish. The sample dried at 300° worked practically the same as the one heated to 200°. Hence, it was obvious that whatever changes had taken place in the structure of the clay occurred at about 200°C, and this was the temperature chosen in the work that followed.

In order to bring out the changes caused by this drying treatment, still further experiments were made. A sample of the undried clay was taken and divided into two parts. One-half was dried at 200° in a laboratory oven, the other half was left as it was. Both of these batches were placed in porcelain jar mills of one gallon size, together with sufficient distilled water to make a fairly thick slip, and ground for one hour. The grinding action of these small mills is very slight so that the fineness of grain was affected but little. Each of the two slips was passed through an 80-mesh sieve.

The viscosity of each of the slips was then determined by means of a Coulomb viscosimeter which had been constructed in the Department of Ceramics, University of Illinois, for the purpose of studying clay slips, as described in Vol. X, Trans. Am. Ceramic Society.

The amount of clay held in suspension in the slips was determined by evaporating the slips to dryness and weighing in small metal pans. In order to obtain the viscosities

of lower concentrations, the slips were diluted with water, thoroughly stirred up and tested as before.



In the accompanying curves we observe clearly what great changes have been brought about by the drying treatment. It is evident that this change involves the structure of the colloidal portion of the clay, since naturally neither the size of grain was altered nor anything added to or subtracted from the clay in drying. Just how long a time would be required to bring back the clay to its original state of viscosity, if this is possible at all, would be an interesting question.

We observe from the curves that for instance in the case of the fresh clay a viscosity of 1.18 is reached with 20% of clay, while for the same viscosity 35% of the dried clay is required. The latter therefore shows a marked decrease in the viscosity characteristic of plastic clays.

In order to bring out the differences between the undried and the dried clay still further, another series of

tests was made by taking these clays alone and in several proportions and making them up into round discs, 3¼ in. in diameter and 7/8 in. thick. For this purpose the fresh clay was thoroughly wedged, while the dry clay was pulverized and passed through a 10 mesh screen, made up with water and tempered. The discs were made by batting the clay into a slab between two guides and passing a roller over the latter so as to obtain uniform thickness. The slabs were then cut into discs by means of a tin biscuit cutter and when sufficiently stiff they were repressed on a hand screw press provided with a corresponding round die. Ten trials of each series were placed in a Seger voluminometer and the volume determined by displacement in kerosene after having been immersed in petroleum for 24 hours. The same process was repeated after the discs were dry. The average of ten determinations was taken as the drying shrinkage. The dry test pieces were all placed in a Caulkins muffle kiln, fired with oil and burnt to cone 4, this temperature having previously been determined as the best maturing point of the clay. Each of the ten trial pieces of the several series which had been measured for drying shrinkage, was, after burning, again placed in the voluminometer and the volume determined. The balance of the trials were placed in water with one face exposed and allowed to stand for 48 hours, this period of time having been established as the point beyond which practically no further absorption took place. They were then divided into classes according to the absorption found.

At the same time discs were made in similar manner from Galesburg shale which, however, were fired at cone 2, the best temperature for this material. The results of this work are collected in the following tables, the shrinkage being expressed by per cent in volume. The percentages of loss are based upon 200 discs made from the undried Urbana clay, 200 of the dried Urbana clay, and 125 discs of A, B, and C.

KIND OF MATERIAL	Urbana Clay not dried	Urbana Clay dried at 200°	Urbana Clay 25% dried, 75% undried	Urbana Clay 50% dried, 50% undried	Urbana Clay 75% dried, 25% undried	Galesburg shale
MARK	U	UD	A	B	C	G
Amount of tempering water, in %, of dry wt.	33.5	29.9	32.0	31.9	31.0	....
Drying Shrinkage in %, by vol.	41.2	29.3	39.1	35.8	34.1	7.5
Burning Shrinkage in %, by vol.	21.1	20.6	21.0	21.0	20.9	16.2
Drying loss in %	32.0	0.5	26.0	15.3	9.7	....
Burning loss in %	15.0	4.0	9.1	11.0	12.9	2.5
Total loss in %	47.0	4.5	35.1	26.3	22.6	2.5

From these results it is apparent that the pre-heating of the clay has greatly decreased the drying shrinkage, the difference being 11.9 per cent in volume or nearly 4 per cent in linear shrinkage, assuming for practical purposes that the linear shrinkage is one-third of that in volume. A curious fact is also the decreased burning shrinkage, so that the total shrinkage is decreased from 62.3% by volume to 49.9%, resulting in a difference of 12.4%. Or, expressed in linear dimensions, the decrease in total shrinkage is from 20.7% to 16.6%. The loss in drying which took place in the open laboratory at ordinary room temperature has been decreased from 32.0 to 0.5%, a gain of 31.5%. The gain in burning loss was 11% and in the total loss 42.5%.

As to the mixtures of preheated and undried clay, we observe that the shrinkage and losses decrease roughly with the increase of preheated clay and thus these results verify the observations on the preheated clay itself.

Since there is a possibility from the practical standpoint of the drying and burning losses that the same results would be obtained by the addition of sand to the clay, a short series was carried through in which 5, 10 and 15% of sand passing the 8-mesh sieve were added to the undried Urbana clay. Of each sand mixture 125 discs were made.

The results of this work are collected in the following table in which the data for the undried and the preheated clay are repeated for the sake of comparison:

KIND OF MATERIAL	Urbana Clay not dried	Urbana Clay dried at 200°	Urbana Clay undried: 95% clay, 5% sand	Urbana Clay undried: 90% clay, 10% sand	Urbana Clay undried: 85% clay, 15% sand
MARK	U	UD	D	E	F
Amount of tempering water, in % of dry wt	33.5	29.9	32.0	31.5	31.1
Drying Shrinkage in %, by vol	41.2	29.3	39.1	37.6	35.2
Burning Shrinkage in %, by vol	21.1	20.6	20.2	19.3	18.6
Drying loss in %	32.0	0.5	6.1	5.2	5.0
Burning loss in %	15.0	4.0	11.3	33.0	42.0
Total loss in %	47.0	4.5	17.4	38.2	47.0

From these results we observe that the drying shrinkage has been decreased somewhat and the drying loss a good deal, roughly by about 25%. The burning shrinkage also has been reduced, but unfortunately the burning loss, though showing an improvement in the 5% sand mixture, increased very rapidly with more sand. As compared with the total loss of the preheated clay, the gain has been but small and at least as far as the sand used was concerned this remedy offers but little hope for practical improvement since the losses are still too great. The advantage of preheating this joint clay is seen from the small loss in drying and burning. An explanation of the ineffectiveness of the sand mixture perhaps is due to the fact that the clay itself is not changed in its physical properties and we have here simply a case of dilution. With larger amounts of sand we also have in burning certain volume changes which appear to be opposed to each other, so that strains are produced which result disastrously.

In order to show whether the Urbana joint clay after having been burnt apparently to a sound body really was free from incipient checking, it was determined to make rattler tests. For this purpose the burnt discs, free from flaws, were first graded according to their water absorption and compared with discs made from Galesburg shale which had burnt to the best degree of maturity.

The rattler test was made in a Scheibell mill, consisting of a chilled iron receptacle, elliptical in cross section, with a long axis 23 in. in length and a short axis of 7½ in., revolving 31 revolutions per minute. The rattler was first standardized with a mixture of iron jackstones in the shape of 1¼ in. cubes weighing on an average 0.9 pound and Iceland pebbles with an average length of 3⅛ in. and a width of 2⅜ in. The average weight was 0.7 pound. In the standardization the Galesburg discs were used, five of them in a charge which weighed about 2.2 pounds. The combination giving the most constant results was used for the comparative tests of the joint clay discs with the Galesburg test pieces. In each case the results were checked. Finally, two charges were used, 2-C, containing 75 pounds of pebbles and 50 pounds of jackstones and 2-D, consisting of 100 pounds of pebbles and 50 pounds of jackstones. In using charge 2-C the mill was about ⅗ full and with 2-D it was ⅘ full. The time of running was one hour. It was found that 2-C was a more severe charge than 2-D on account of the element of impact introduced by the mill being less full.

The rattler losses are tabulated as follows:

All discs apparently perfect and showing an absorption of 1% and less.....	2—C		2—D	
	% Loss		% Loss	
Galesburg shale, G.....	9.8	9.7	5.5	5.5
Urbana clay, preheated, U. D.....	12.3	12.8	4.0	4.5
Urbana clay, not dried, U.....	14.7	14.5	5.0	.....
25% preheated & 75% undried Urbana clay, A..	11.5	.....	.....	.....
50% preheated & 50% undried Urbana clay, B..	11.8	.....	.....	.....
75% preheated & 25% undried Urbana clay, C..	11.8	.....	.....	.....
95% undried Urbana clay, 5% sand, D.....	12.5	.....	5.9	.....
90% undried Urbana clay, 10% sand, E.....	12.5	.....	6.2	.....
85% undried Urbana clay, 15% sand, F.....	14.1	.....	7.4	.....

These results show plainly that preheating has improved the resistance of the joint clay to abrasion decidedly, not, of course, due to any change affecting the mineral and chemical structure of the clay itself, but to the elimination of drying defects, incipient cracks and strains caused in drying. If it were possible to dry the fresh clay without injury it would possess the same resistance to abrasion exhibited by the preheated material. The Urbana clay is evidently more brittle than the Galesburg shale, but it is harder, due to the fineness of grain of the joint clay. One might venture to say, judging from the above comparison, that the latter could probably be used as a paving material for streets which are not subject to heavy travel, provided, however, that the clay would correspond uniformly to the sample tested in this work, which is somewhat questionable in the case of glacial deposits.

The addition of sand, according to the above results, contributes nothing to the resistance to abrasion, though it shows an improvement over the undried clay by lessening the checking in drying.

CONCLUSIONS.

From the results of this work it is evident that the faults of the joint clay have been overcome by this preliminary drying treatment at 200°C. The sticky nature of the clay has been destroyed, the drying shrinkage reduced greatly and the burning shrinkage partly, while the losses in drying have been practically eliminated and the burning loss lowered most decidedly. If, therefore, this preheating can be carried on economically in properly constructed dryers, either fired directly or making use of the waste heat of kilns, the treatment thus suggested ought to find more extensive practical application.

At the same time there must be remembered that the dry clay can be disintegrated and screened more cheaply than the clay coming wet from the bank, thus enabling the manufacturer to remove the impurities, such as gravel,

lime, pebbles and other mineral detritus, which are especially liable to be present in the glacial clays, more cheaply and thoroughly, besides making the operator independent of weather conditions. Also it is thus possible to produce wares of a higher grade from low grade material and in districts where other clays are lacking. It is self-evident that the increased cost of production caused by this treatment may be prohibitory in localities where it is possible to find clays which do not require this kind of preparation. The matter of the preliminary drying of clay is not new, but the changes brought about by it have not been clearly recognized and its importance in certain cases not considered. It ought to be especially applicable for higher grades of ware such as roofing tiles, hollow ware, terra cotta, etc.

In regard to the cost of drying clays by the rotary dryer, which is the most efficient apparatus for this purpose, some data have been obtained from two firms, A and B.

Firm A recommends a rotary dryer, heated by direct firing, 60 in. in diameter and 40 ft. long. This aparatus is encased in brick. The clay is fed automatically and at a constant rate, this being very important. About 35,000 common and from 5,000 to 6,000 fire brick are required in the construction. The total weight of the dryer is about 40 tons. The cost of the dryer, complete, is $3000, to which the freight is to be added. This machine will dry 15 tons of clay per hour. It will require 8—12 horse-power to operate and for a material containing 15% of moisture the fuel consumption would be about 500 pounds of coal per hour, at the rate of 15 tons of clay for the same length of time. Including labor and depreciation the cost of drying is estimated at 10 cents per ton.

The firm B estimates the cost of the dryer to be $3,500 and cost of erection at $600. The power required is 20 horse-power and the fuel consumption 60 pounds of good coal per ton of bank clay. The cost of drying is estimated to be 12 cents per ton of bank clay.

In this connection we must remember also that the size of the brick moulds, etc., must be reduced in order to correspond to the decreased shrinkage of the preheated clay, though this does not mean that a saving is effected.

Further work is necessary to determine to what extent this method may be applied to materials other than the joint clay discussed in these tests.

Practically all the laboratory work of this investigation was done by the junior writer, Mr. F. E. Layman, the senior writer having planned the experiments and assisted in writing up the results. The means for carrying on the tests were furnished by the Ceramic Department of the University of Illinois, through Prof. C. W. Rolfe, the director.

CAN WATER FROM THE CLAY PRESS BE RE-USED?

BY

THOMAS GRAY, East Boston, Mass.

I find nothing in any paper or discussion of the American Ceramic Society on this subject. Unfortunately, I can say nothing on this point from experience, having never tried to re-use filter-press water on account of hearing adverse reports. A large saving could be made by re-using the water and perhaps the bacteria thus preserved would be a simpler means of developing plasticity than by the artificial process of tannin, straw, etc., as recommended by some.

The objection I found, upon inquiry, was that in re-using water, alum collected and caused cracked ware. By re-using it will certainly age the water, and (if that is desirable) collect the bacteria to toughen the clay, to make better ware, which is the point desired by Mr. Stover, as shown in his articles, Vol. 4, 183; Vol. 5, 358, and by Mr. Acheson, Vol. 6, 31, and by Mr. Minton, Vol. 6, 231.

Is it safe to re-use water, or can it even be re-used twice?

If it can be, how often?

What is the effect of re-using, and why?

Mr. Orton: This is strictly a note for discussion. Mr. Gray does not attempt to state any facts, but postulating various conditions, asks what the results would be. I hope some of you will answer these questions.

Mr. Hope: We use the water over many times—dozens of time, with no ill results.

Mr. Stover: I do not think it is a question that can be answered by "yes" or "no". It depends largely on the composition of the mix. If you have soluble salts coming

off from the filter press, as we had, you cannot use it. We had to abandon the re-use of the water on that account. If there are no soluble salts, it will be more apt to be a safe proposition. If you have soluble matter which goes off in solution, you increase the concentration every time you use it.

Mr. Orton: Mr. Ashley once made a statement to me, which bears on the point. In discussing his process for grading the color of white clays by comparison with a series of standard mixtures, I asked him if he used the same water over and over again in preparing clay bodies for the shop and he said not. I then asked him if he did not find considerable darkening of the color of the white ware body-clay, by putting in the muddy Ohio river water fresh with each mixing. He said he used to think he did, before he got an accurate way of measuring color, but that he found it was actually much less than he had thought, and that the difference in the color scale did not exceed *one point*. This scale was prepared from the whitest clay he could find, mixed with a strongly colored or yellowish ball clay. Between these two extremes, 100 points, or mixtures corresponding to one per cent changes in proportion were prepared. He said the color of a body was off only about one point, as a result of the use of Ohio river water, which is at times strongly yellow and muddy. So it is likely that many of us have been giving undue weight to the advantages of using the perfectly transparent water from the filter presses. If that statement can be borne out by the experience of others, it is important.

Mr. Stover has pointed out that there can be no "yes" or "no" answer to Mr. Gray's questions. Much depends on what kind of clay you are washing. I have seen yellow-burning clays thrown out to weather before use, in which the salty matter, chiefly sulphates, had accumulated to such an extent that when the wash water was used over and over again it became practically a saturated solution of sulphates of lime, iron and alumina. In a

case like that, the use of the same water over and over would result in severe difficulties, not only with the ware, but with the moulds. The growth of crystals from the clay-body into the pores of the mould would make it almost impossible to loosen the ware from the mould, and would tend to tear up the surface of the mould as well. I have seen moulds in this shop covered with a growth of fuzzy needle-like crystals from an eighth to a quarter of an inch long, like a two weeks' growth of beard.

Where the amount of saline matter in a clay is small, I do not think the concentration of soluble impurities from using the same wash-water repeatedly amounts to much. In fact, the same water is not used over very many times.

The clay itself takes out in the wet filter press cakes, a considerable proportion of the water required to slip it. For instance, 1000 lbs. of clay if made up into a slip of 33 1/3 per cent solids, would require the addition of 2000 lbs. of water. If the filter pressed clay as taken from the press consists of 75 per cent clay and 25 per cent water, then the filter press plates will weigh 1333 lbs., if there were no loss in the operation by leakage, etc., etc. In short, one-sixth of the water is removed by the filtered clay each operation, and this amount must be supplied by new water for the next blunging.

The first batch of clay passing through the blunger and press will be greatly purified. Five-sixths of its original saline matter will be removed in the wash water. But if this wash water is again used, it will contain after the second blunging all of the soluble salts of the second charge plus five-sixths of the salts of the first charge, and the clay will contain after filter pressing, one-sixth of this larger quantity of soluble salts, or 11/36 of the quantity of salts it contained before washing. A third charge washed in the filtrate from this clay would again be much less purified than the second. By carrying this calculation on for a time it will be seen that while theoretically there

would always be less salts after washing than before, owing to the fact that the water was pure when the process began. Still the purification attained after 10 or 12 charges is infinitesimal and may be neglected in all practical calculations.

You can readily see therefore, that where the same water is used over and over, being supplemented by so much new water each time as is necessary to replace that taken out by the filter-pressed clay, that there is no real purification of the clay so far as soluble salts are concerned. The salts are simply redistributed evenly throughout the mass. Where they existed in crystalline lumps or masses in the clays, they are dissolved and permeate all portions in the filter press plate. In drying, either the plate or the ware made from it, there is every likelihood of a new local concentration of the salts on the surface, but probably never as irregularly as in the original unwashed clay.

The full benefits of purification by washing can only be secured by using fresh water with each blunger full of slip, and where this is done, a removal of soluble salts amounting to from three-fourths to nine-tenths, according to the dilution of the slip and the water content left in the clay in pressing may be expected. It will depend also somewhat on the purity of the water supply and the nature of the soluble salts. For instance, if the water used is a hard limey river water, well impregnated with calcium sulphate, then it would obviously be impossible to do much purifying of a clay which was well loaded up with this same impurity, for the water would soon become saturated and the impurity would remain undissolved. In clays where the salts to be removed consist of the easily soluble chlorides and nitrates of the common bases and the sulphates of all of the common bases excepting lime, lead and barium, there is no likelihood that the wash-water will become saturated, and purification may be expected up to the degree provided by the mathematical proportions of the filtrate and solid residue.

A PECULIAR PROPERTY OF SOME GLAZES.

BY

ARTHUR E. MAYER, Beaver Falls, Pa.

In the production of a good earthenware or china glaze, one important feature is often neglected. This is the preparation of the glaze, so that it is possible for the dipper to turn out ware that, when fired, will not show a "curtained effect". The curtaining detracts very much from the appearance of the ware, and in case it should have an under-glaze print it will be hopelessly ruined. In addition to this curtaining just mentioned, it has another bad quality that is a great source of annoyance to the dipper, this being its ability to quickly precipitate the glaze to the bottom of the tub. When once there, the grains seem to interlock forming a very dense mass, that can hardly be dug out with the fingers.

The effects of a glaze of this nature are more apparent on a plain edge piece of flat ware, because the glaze will roll in pools around the edge instead of being thrown off. In the case of scalloped edge ware it is not so noticeable, because the scallops cut off the drops allowing them to go back into the tub.

These conditions of a glaze are well known in the Staffordshire Pottery district, and are called "ropey glazes," but in the East Liverpool district it is not so often encountered.

There are many substances that will remedy this objectionable feature in a glaze, such as the sulphates of barium, strontium and magnesium, boric acid, vinegar, blood, milk, syrup, dextrine, gum-arabic, plastic clay and many other things.

We will not discuss the action of these, until we see the condition of our glaze when in this settling state.

It has been noted that after long grinding this condition is most evident, and in order to investigate this, a typical white-ware glaze was taken having the following formula:

.054 K_2O		
.226 Na_2O		
.408 CaO		2.398 SiO_2
.312 PbO	.255 Al_2O_3	.348 B_2O_3
1.000		

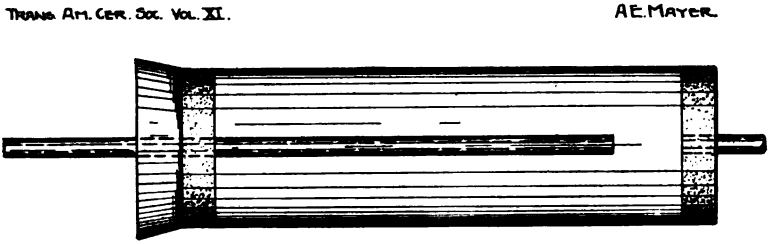
The batch weight is as follows:

Fritt	2830	Grammes
Spar	425	"
China Clay	145	"
Flint	345	"
Lead	1255	"
	5000	"

This 5000 grammes of glaze was put into a small ball-mill (having internal dimensions 10 in. by 12 in.) with 15 lbs. of round flint pebbles varying in size from 1 to 2½ inches in diameter, and making about 45 revolutions per minute.

This glaze was ground wet for 32 hours, and at intervals of 4 hours a sample of about one pint was taken out. This sample was then put into an apparatus for determining the degree of viscosity, which consisted of a straight Welsbach light chimney 4.5 c. m. diameter, with a cork in the lower end and a piece of fine bore glass tubing put into this cork so as to just project to the inside of the chimney. The upper end was closed with a rubber stopper, and a piece of glass tubing ran through it, and to within 3/4 of an inch from the tube in the lower cork. To operate this apparatus, the tube in the bottom cork was closed by the finger, and the chimney filled with glaze-slip, the upper stopper and tube placed in position, and the number of seconds counted that are required to run 200 c. c. of slip. Using water in this apparatus requires

53 seconds to run 200 c. c., and considerably more time is required for the glaze-slip, varying with the viscosity. A full description of this can be found on page 163, Part II, Vol. VI Transactions of English Ceramic Society.

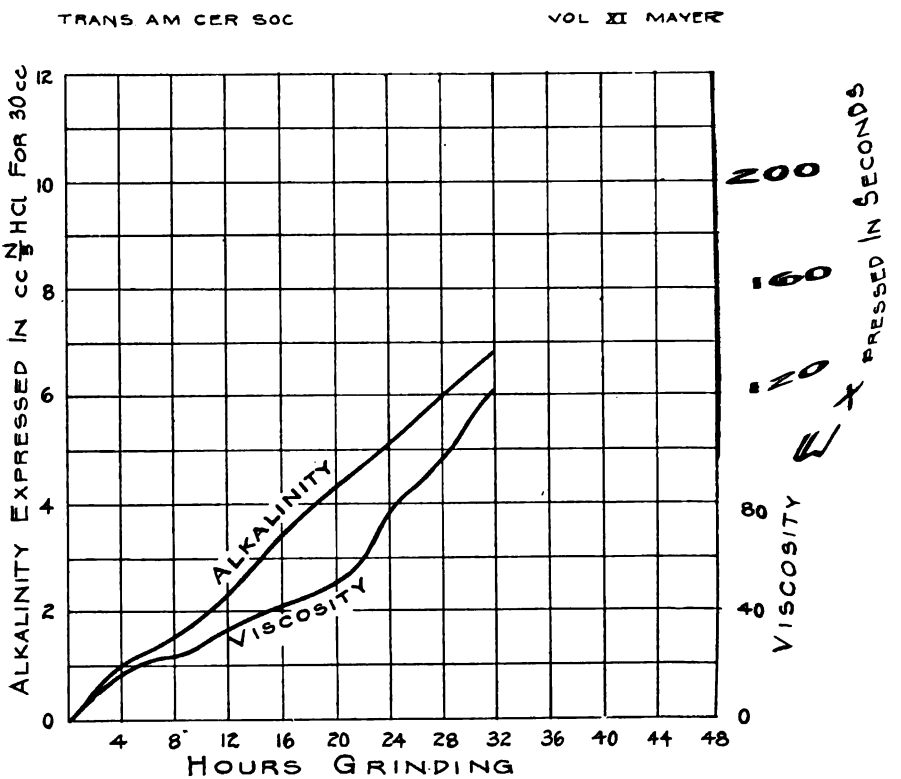


The sample is next allowed to stand for several hours in a covered bowl, then a 30 c. c. sample is taken and alkalinity determined by titration with N_5HCl using phenolphthalein as an indicator.

The following is a table showing hours of grinding alkalinity, viscosity, etc.

Sample No.	Hours Ground	C. C. of $\frac{N}{5}$ HCL for 30cc of SOL	Viscosity in Seconds	Viscosity of Water	Difference in Viscosity	Remarks
1	4	1.	69	53	16	Not ground fine enough to dip
2	8	1.6	77	53	24	Not ground fine enough to dip
3	12	2.5	89	53	36	Not ground fine enough to dip
4	16	3.4	94	53	41	Not ground fine enough to dip
5	20	4.3	105	53	52	Fine enough to dip
6	24	5.1	130	53	77	1st sign of settling properties
7	28	6.1	143	53	96	More sign of settling properties
8	32	6.8	175	—	122	A very bad settling glaze

The above data has been plotted on the following chart:



Notice should be here made of the consistency of the two curves for alkalinity and viscosity. It is here very plainly brought out that the more the glaze is ground the finer the particles, and the finer the particles the greater the alkalinity, and the greater the alkalinity the more viscous the glaze.

This last analogy seems to be the key note to the whole situation.

Now since we have found the state of the water in which our glaze is ground, we can consider better the action of the various named correctives. These correctives seem to be divided first into physical and chemical actions.

In the first group, comprising those whose action on the glaze is physical, we have first, syrup, a thick substance that when put into a glaze tends to thicken it by incorporating its body into that of the glaze, thus giving it more resisting power to keep the fine particles in suspension.

Milk is sometimes used, and under the ordinary temperature conditions of a dipping house soon sours and becomes very thick, thus giving the glaze more body by mixing with it.

Animal blood clots in a few minutes, and thickens, thus acting the same as the two above mentioned items.

Gum-arabic and dextrine go into solutions with water, and act identically as the syrup.

A plastic clay goes into suspension in the water floating the glaze, and thickens it both by the fact that it takes up some of the water to make it plastic, and then intermixes with grains giving the resulting mixture more power to stay in suspension.

All the above named seem identical in their method of action and need no further discussion here.

The correctives having a chemical reaction have to be divided into two classes, those which act directly to give the desired result, and those which by means of chemical reaction give the desired result by physical means.

In the first class we have:

Boric acid:—This is just a case of neutralization of the alkali by the weak acid. From an analysis it was determined that the alkali found in the water in which the glaze was ground, existed as the silicate of soda. The acid acts on the silicate of soda forming some neutralized sodium compound.

Vinegar:—By means of this substance acetic acid is introduced with a neutralizing effect.

Nitric, sulphuric and hydrochloric acids are sometimes added for the purpose of neutralizing the alkali existing in silicate of soda.

It seems rather a bad practice to introduce an acid like vinegar into a glaze that contains lead (as most all do), because any in excess of that required for neutralization is liable to form acetate of lead, which is very poisonous, and endangers the life of the dipper.

Many of the glazes such as are used in East Liverpool, in which boric acid and flint alone are fritted, never show this settling property, because on grinding, a great quantity of boracic acid is set free thus neutralizing any alkaline properties.

Within this chemical action division we have a group of sulphates of barium, strontium and magnesium, in which a double action occurs, giving greater advantage than any of the former. The alkali existing as silicate of soda is precipitated as the silicates of the various metals, according to the following reaction.

$$Mg\ SO_4 + Na_2\ SiO_3 = Mg\ SiO_3 + Na_2SO_4$$

By this reaction we do away with the alkali causing the trouble, and have remaining a gelatinous precipitate of silicate of magnesia acting as much as soured milk or plastic clay.

The commonest of these salts is the sulphate of magnesia, and the one ordinarily used for this purpose.

On the face of it and according to theory, it would be a mistake to introduce a sulphate into a glaze, because of the danger of scum. The theory here however does not hold, because at this pottery we have used one-half per cent of sulphate of magnesia in our glaze for two years, and have never in that time had a piece of scummed ware from this cause.

In conclusion I would say a "ropey" or settling glaze is caused by the presence of too much alkali liberated, often due to fine grinding. This can be corrected by either chemically neutralizing by means of acid or physically by means of some substance to give the glaze more body.

THE HUMIDITY SYSTEM OF DRYING.

BY

E. D. GATES, Seattle, Washington.

The desire to find a method of drying architectural terra cotta more quickly, and at the same time more safely and more economically, led the writer toward this subject some eighteen months ago.

Ware which has been cracked in drying is seldom seen around an aggressive clay plant, unless a sudden rush of orders causes a shortening in the established period of drying, in which case you are all no doubt familiar with the sad results.

In the present quickening days of the clay industry we are forced to continually increase the output of our plants, and as few plants are so arranged that all departments have the same output, the result is that one or more of the departments are compelled to rush the product through their stage of production in order to keep pace with the remainder of the plant. You can probably recall having seen this occur many times in different plants.

In some cases this will be due to the limited kiln capacity, in others it may be the machine or shop, while in still others it may occur in the driers.

We all object to bringing our ware safely to the driers and then have to remove a good proportion of it with shovels — the loss is great. In the case of terra cotta the ware at the drier door represents about 53% of the total cost. If this is reduced to scrap the greater part is loss.

It so happened that the driers of our plant were too small to give the ware the slow drying it required, and with a sudden rush of work it became necessary for us

to either increase the capacity of the coils which were already installed or to add to them. The latter was not practical at that time so another method had to be found.

Having always known that the pieces of terra cotta on the coils began to dry on the corners and projecting parts before the remainder of the piece was warm, unless these corners were covered with paper or sacking, and knowing that this resulted in unequal shrinkage with the attendant cracking and warping, started me on a train of thought which led to the following experiments and to this method of treatment.

It seemed to me that the proper method of procedure would be to heat up the whole piece of clay ware to the temperature reached in drying before any drying could commence. The hygroscopic moisture, or water mixed with clay, would then leave the whole piece of ware quite evenly and from all portions at once, thus making it shrink in all parts at the same time and at the same rate, doing away with cracking and warping and increasing the percentage of good ware.

It also appeared that if this could be done the capacity of the driers would be largely increased.

It was decided, after giving the matter careful thought, that the best, if not only manner of accomplishing this, would be by properly controlling the humidity of the air in the driers until the pieces had become heated, and then allowing actual drying to commence.

As worked out for commercial purposes this would consist in introducing live steam into the driers, while the temperature was being raised, care being taken to keep the percentage of humidity so high that the air in the drier could not take up any of the moisture that the ware contained. The pieces of ware would therefore not be able to dry any until the humidity was allowed to drop. This condition would be carefully avoided until the ware had reached the temperature of the drying chamber. This being accomplished, the injection of steam could be

stopped and air allowed to pass through the steam coils and drier and carry off the water contained in the pieces. The live steam injected would aid in heating the drying chamber and so facilitate the operation.

It appeared that this method would permit of holding our ware without the shrinking being allowed to start, until it was thoroughly heated to the temperature desired. Acting on this assumption, we equipped two driers as follows:

Each drier contained three coils, of about 400 lineal feet of one inch pipe each. Over each set of three coils we erected boxes, the boxes being equipped with sliding doors on the side for the purpose of loading and unloading the coils. Suitable openings were provided at the top and bottom for the inlet and outlet of air, these openings being arranged so that the amount of air could be controlled.

For jet pipes we used one-half inch steam pipe having a hole one-eighth inch in size every foot, and when installing these jet pipes we were careful to have all the holes in line. These jet pipes were first installed near the top of the boxes with the holes turned up. This was thought to be the proper place for them owing to that being the hottest part of the boxes and the air in that part being able to take up the greatest amount of moisture. This location of the jet pipes was subsequently changed and they were placed under the coils near the floor. The change being made to overcome the dripping of water upon the ware from the roof of the boxes, the steam condensing when it struck the comparatively cold roof surface. This last location was found to be much better as the pipes were not only out of the way but the steam could humidify the air as it passed up through the coils and becoming heated was hungry for more moisture than it contained on entering.

When first tried, over a year ago, the operation was carried on in the following manner:

The coils were loaded with green ware, the doors closed and the steam turned on the coils, gently at first.

The hygrometer was then consulted and the humidity kept as near 80% as was possible. We found that oversaturation would occur in parts of the drier if the humidity was allowed to run much over 80%, so that was the percentage adopted in practice. The attention of the operator was required for a short time as the drying chambers raised in temperature, the admission of steam being increased as was necessary to hold the humidity near the allowed 80% and the steam on the coils being also increased.

In order that the heat of the coils could be accurately controlled we finally arranged each two inch pipe feeding the coils, with a one-half inch pipe and valve for a by-pass by the two inch valve. This was found to be a good arrangement, as it allows the steam to be controlled so that only hot water can enter the coils when low heat is wanted, and at the same time the valves are not cut out by the steam as would be the case if they were only partly opened. In several hours, after the ware had become heated, it was our practice to decrease the amount of steam injected and open the upper and lower air holes and thus allow the drying to start. The steam jet being left on a little as a precautionary measure to avoid too rapid drying.

The necessity of crowding our driers having been overcome, the use of the system was discontinued for several reasons. Prominent among them was the fact that I had not been able to carry out the experiments necessary to a proper understanding of the best manner and time required to get the maximum results from its use. These experiments would, of necessity, have to be carried out on a small scale at first and the knowledge thus gained could then be applied to the operation of the large driers and a schedule worked up that would give the amount of steam allowed on the coils, the humidity per cent. the regulation of the valve controlling the jet and the length of time necessary for each stage of the process, as well as the amount of air to be admitted and passed through the driers after the heating up was accomplished. All the in-

formation, in fact, that would enable any intelligent man to successfully carry the ware through the drying stage with safety and despatch. The experiments given later were performed with this end in view and to also determine how the system would act with other classes of clay products to see if the method was adaptable to other lines besides architectural terra cotta.

The small drying chamber, for these experiments, was roughly built so as to make the conditions as similar as possible to those met in actual practice. It was three feet long by two feet wide and two feet high and had glass on the front and back to enable us to read the thermometers and properly observe the conditions and action of the piece of clay ware to be dried. The box was equipped with a steam coil consisting of 10 lineal feet of three-quarter inch steam pipe and a jet pipe made of one-half inch pipe with one-eighth inch holes. This jet pipe was laid on the bottom of the box under the steam coils and the holes turned downwards so that the steam would spread as much as possible before rising and passing up through the coil.

In some of the experiments a hygrometer was used in each end, while in others only one was used. However, in all of them a thermometer was imbedded deeply in the clay body so that its actual temperature could be known at all times.

The experiments run were as given below:

No. 1. Piece of terra cotta, on its back or bond with slats running lengthwise; jet used.

No. 2. Piece of terra cotta, on bond; slats crosswise; jet used.

No. 3. Piece of terra cotta, on bond on a board having holes; using the jet.

No. 4. Piece of terra cotta, on bond on board without holes; using the jet.

No. 5. Piece of terra cotta, on bond, on slats lengthwise; without using the jet.

No. 6. Solid fireclay block, on slats lengthwise; using the jet.

No. 7. Same as No. 6, but allowing more time to heat the block.

No. 8. Shale body, about brick size, on slats lengthwise; using the jet.

No. 9. Fireclay mixture containing grog, on slats; using the jet.

Also a cube of terra cotta body in the box at the same time.

The data kept consisted of the time of day, the time in minutes from the start, the temperatures of the wet bulb and the dry bulb thermometers, the per cent of humidity, the number of degrees Fahrenheit raised in each 15 minutes, the condition of the piece, the temperature of the piece as indicated by the thermometer imbedded in it, the shrinkage, the condition of the jet and any remarks. We also determined the water content of some of the pieces and care was used to see that all the samples of terra cotta contained approximately the same amount. They were all taken just after being removed from the mould and were quite wet.

The bodies experimented on were all such as required a good deal of care in drying. The large blocks were made of a body which is particularly difficult to bring through the drying without cracking. The results of the experiments and the manner of running them which follow are greatly condensed, only the important facts being given, so that the conclusions reached may be seen.

You will note that we succeeded in raising the temperature of bricks about one degree every two minutes, on the average, while in most cases in the early part of the treatment we could raise it a degree a minute without cracking them.

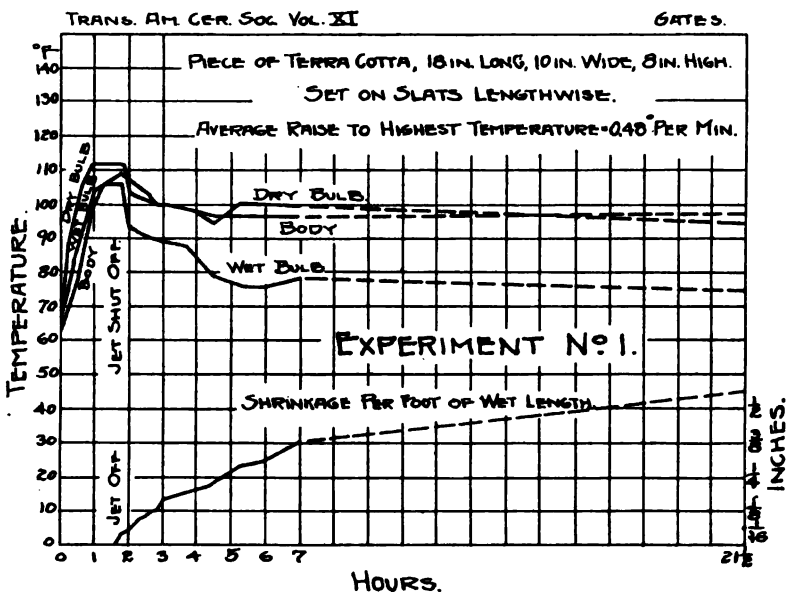
EXPERIMENT No. 1; using the jet.

Piece of terra cotta, 1 foot 6 inches long, 10 inches wide and 8 inches high, set on its hollow or bond side on slats running lengthwise and using the jet to control hu-

midity. The piece was quite wet having been out of the mould only a short time.

Started at 10.30 A. M. and finished at 8 A. M. the next morning.

The temperature of the drying chamber at the start was 66° on both the wet and dry bulb thermometers. This temperature was raised to 112° in one hour and held



there. The initial temperature of the piece was 62° and it was raised 48 degrees to 110° in one hour and forty minutes, the average raise being .48 degrees per minute.

The clay body was dried, without cracking, in 19 hours and 45 min. after turning the jet off, making a total time of 21 hours and 30 minutes to get a shrinkage of 9/16 inch per foot. The piece was perfectly true in shape when dried.

EXPERIMENT No. 2; using the jet.

Piece of terra cotta, same in size as that used in No. 1, was placed on the bond on slats running crosswise. This piece was quite soft.

The chamber thermometers showed 74° on the wet bulb and 88° on the dry bulb at the start. This was raised to 124° in 2 hours and 15 minutes and held at that point. The thermometer in the body showed that it had an initial temperature of 62°, which was raised 50 degrees to 112° in 2 hours and 15 minutes, the average raise being .37 degrees per minute.

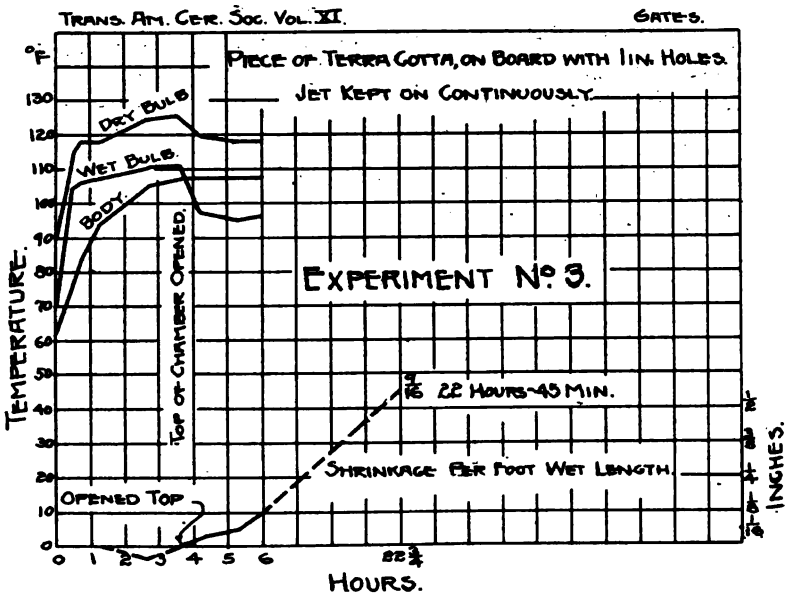
The total shrinkage was 9/16 inch per foot but the piece was cracked through the center vertically, due it seems to the slats under the piece running across the direction of greatest shrinkage and the body not crawling as easily as it would if the slats were arranged as in the first experiment.

EXPERIMENT No. 3; using the jet.

Piece of terra cotta, same as in Nos. 1 and 2, set on a regular board having one inch holes bored through it to allow the air and heat to get at the inside of the piece.

At the start the hygrometer registered 70° on the wet bulb and 90° on the dry bulb. This was raised to 125° in 2 hours and 15 minutes. The temperature of the body at the start was 62° and was raised 46 degrees to 108° in 3 hours and 5 minutes, an average raise of .24 degrees per minute.

The piece was dry in 22 hours and 45 minutes from the time of placing in the box and was perfectly true and was without cracks. The total shrinkage was 9/16 inch to the foot.



EXPERIMENT No. 4; using the jet.

Piece of terra cotta, same size and shape as before, on bond on board without holes in it. The piece was therefore protected from the circulating air on the bottom side, and the ends and sides and the top were exposed.

The temperature of the box was 67° on the wet bulb and 84° on the dry bulb at the start. The dry bulb temperature was raised to 119° in 5 hours and held at that point. The temperature of the piece was 60° at the start, and was raised 31 degrees in six hours and fifteen minutes to a temperature of 91°. The jet was then shut off and the steam coil kept on. In 23 hours and 30 minutes the temperature of the piece was 94° and the shrinkage ½ inch in one foot.

At the end of 30 hours from the time the piece was put in the drier it was thoroughly dry and had shrunk 9/16 inch in one foot. The piece was in perfect condition as to cracks and trueness of lines.

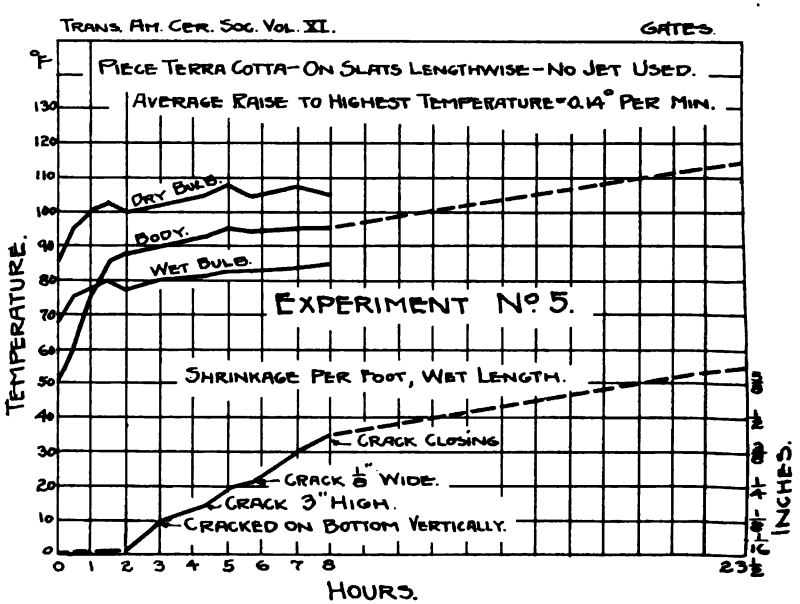
EXPERIMENT NO. 5.

This piece was dried without using the jet.

The piece of terra cotta was the same in size and shape as those used in the previous experiments and was placed on the bond on slats running lengthwise, the conditions being as near like those in Experiment No. 1 as could be obtained. The object being to illustrate the difference in the drying time under the two systems.

The hygrometer at the start registered 68° on the wet bulb and 84° on the dry bulb and the temperature was raised to 108° in 7 hours and held at that point. In experiment No. 1 the box temperature was raised to 112° in one hour.

The initial temperature of the piece was 52°, this was raised to 114° in 23 hours and 30 minutes and the piece was fairly dry at that time. It was however cracked in five places and was unfit for use.



EXPERIMENT No 6; using jet.

Piece of body which is very difficult to dry. Size 17 1/2 inches long, 10 1/4 inches high and 10 1/4 inches wide in a solid block of clay.

The temperature of the box was 65° on the wet bulb and 78° on the dry bulb at the start. This was raised to 112° in 3 hours from the time of starting.

The piece was 42° at the start and was raised 44 degrees to 86° in 5 hours and 45 minutes, an average raise of .127 degrees per minute. At this point the jet was shut off and air allowed to pass through the drier and at the end of 19 hours the piece had risen to 92°. Badly cracked, so the following experiment was tried.

EXPERIMENT No. 7; using the jet. Same size and kind of piece as that in preceding experiment.

The box at the start was 51° on the wet bulb and 60° on the dry bulb and the temperature was raised to 164° in 7 hours and 15 minutes.

The piece was raised from 36° at the start, to 117° in 9 hours. The raise being 81 degrees or an average of .15 degree per minute. The piece at this time had begun to show cracks which must have been due to expansion as there has been no shrinkage in the body. The jet was then shut nearly off and the temperature kept on until a total time of 26 hours had passed. At the end of this time this piece had shrunk 9/16 inch in one foot and was badly cracked.

EXPERIMENT No. 8; using jet.

The body tried was a very stiff shale body, 6 inches by 4 inches by 3 inches in size.

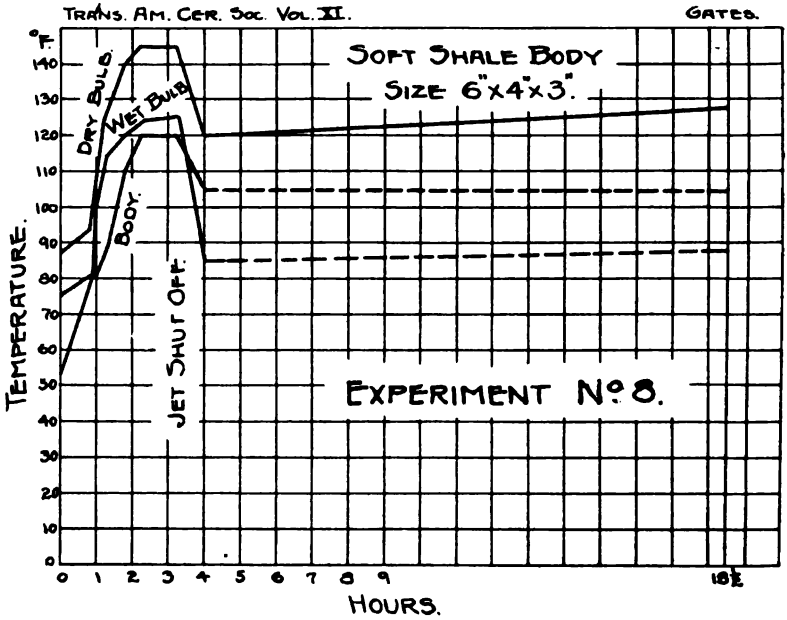
The box at the start showed 76° on the wet bulb and 87° on the dry bulb and the temperature was raised to 146° in 2 hours and 15 minutes.

The piece was 53° in temperature at the start and this was raised 67 degrees to 120° in two hours and 15 minutes, the average raise being nearly .5 degree per minute.

The temperature of the piece had dropped to 104° in 18 hours and 30 minutes and it was dry, with a shrinkage of 3/8 inch to one foot.

The piece showed some fine cracks in the top.

A solid block of the terra cotta body, about 6 inches by 6 inches by 6 inches in size was put in the drying chamber with the shale body but no temperature readings were kept of it. At the end of the 18 1/2 hours it was dry and in good condition.



EXPERIMENT No. 9; using jet.

This body was a fire clay mixture containing 20% grog, and was a brick in size.

The chamber temperature was 82° on the wet bulb and 106° on the dry bulb at the start, it was raised to 148° in one hour.

The temperature of the brick was 60° at the start and it was raised 60 degrees to 120° in 1 hour and 15 minutes without shrinkage. The jet was then shut completely off and the piece allowed to dry. At the end of 6 hours and 45 minutes it was down to 108 degrees and had shrunk 3/16 inch in 6 inches or $\frac{3}{8}$ inch to one foot. It was nearly dry and had not been cracked.

The conclusions drawn from these experiments and from the use of this method in the large driers, are as follows:

(a) That a clay body can be heated up more quickly and safely in the presence of high humidity than is possible when low humidity is kept.

This is shown clearly by a comparison of Nos. 1 and 5.

(b) That a clay body can be raised to a higher temperature in high humidity atmosphere than in low humidity.

(c) That actual drying will start sooner if the piece has been preheated.

(d) That the time of drying can be shortened considerably by this method.

(No. 1 was dried in 21½ hours, by using the jet, and without cracking the piece, while No. 5 was given 2 hours more, without jet, and was badly cracked.)

(e) That drying can be controlled and started or stopped at any temperature by regulating the humidity of the air in the drying chamber.

(f) These experiments also show that some bodies will expand and crack from that cause if heated too rapidly. The clay in question will crack on the brick cars before being run into the tunnels.

It also appears that the body is more quickly, safely and easily heated if the water content is large than will be the case if the clay is rather stiff. This also aids in shortening the time of production.

We hope, in future experiments, to successfully dry the difficult body which was used in Nos. 6 and 7 by heating it slower and so avoiding the cracking which seems to be due to expansion.

Before closing I wish to express my thanks to Mr. J. R. Miller, our General Manager, who kindly permitted me to present this report of these experiments.

DISCUSSION.

Mr. W. D. Gates: I will say here that in September I called in to see the boy at Seattle, and when he showed me the clay he was using I would hardly believe him. It was the strangest variety I ever saw. They mined them from cracks in the hills, which he showed me one rainy day—and I had seen enough long before the day ended. The fissures in the hills are filled with a material such as I had never seen before, looking like great boulders of granite. You can whittle it up with a knife, showing little spots of different colors in it. If the old man had gone out there, I am free to say, he would have quit before he started to make terra cotta out of that. In other words, the boy was up against making terra cotta out of what he had and he took this means of doing it. He accomplished the end he went after, though the results as shown here are somewhat meager. But on thinking it over, it has occurred to me that it is just what the brick men are doing with their tunnel driers, where the ware goes in at the moist end and gradually gets into a drier and hotter atmosphere. I am doing some experimenting at the old ranch on the same line, but the constancy with which my efforts are being required at the other end of the business, getting jobs and keeping up the payrolls, has tended to retard my experimental work. However, I think I will have some results later on.

Mr. Hope: I will say that in the making of hotel china, heavy ware, we have had considerable trouble in the ware cracking in drying. This refers to thick ware

only. It occurs to me that this system of Mr. Gates might be applied to that case to some extent. The cracking occurs when the drying is done too rapidly. Taking considerable time, as this does, might be of benefit.

Mr. Purdy: Drying in the moulds?

Mr. Hope: No, after being taken out of the moulds.

Mr. Simcoe: Referring to large-sized pieces of porcelain, or pieces with great thickness, there is considerable difficulty in properly drying large pieces for the insulator business. The original chunk for bushings has a thickness of from four to four and one-half or possibly five inches solid clay, and you can readily understand the difficulty there. The custom has been to put it in a temperature of about 70 degrees and allow it to stand for two or three days, or possibly more; then put it into a room and gradually bring the temperature up to 110 or 112 degrees and let it stay there. I would certainly like to hear from anybody who has had experience in drying large blocks of porcelain. The process which Mr. Gates has detailed seem to me might be of benefit along this line. I should like to try it and hope I may.

Mr. Stover: The porcelain man seems to be slow to try anything new. I talked with a man who claims to be an engineer in the line of drying, but who confines his efforts more particularly to the wood industry, and he had put in many kilns for drying lumber. He said that in putting green lumber into the dry kiln the only way to get satisfactory results was, first, with moisture, second, with high temperature, and third, withdrawing the moisture. He said that the hardest wood to handle is hickory, but he got it to the point where he could put in eight or nine inch hickory and dry it in half the original time in this way, by using steam. That was eight or nine years ago, and when I brought the matter to the attention of people in Trenton, they said, "Oh, that's wood; it is an entirely different proposition", and I never had a chance to try it, though I was convinced that benefit might be secured by

applying the principle to our line. I am glad, indeed, that this paper has been presented this morning.

Mr. Ashley: I notice that in the case of the fire clay there was an expansion and cracking when introduced into this warm, moist atmosphere. It seems to me the fire clay was insufficiently aged or worked and absorbed in the dryer the water it naturally requires to develop plasticity; consequently, that unless the clay is properly aged and worked, until thoroughly uniform, it is not suitable for this humidity treatment.

SOME LATER NOTES BY THE AUTHOR, MR. GATES:

It will be noted, by reference to the experiments and charts, that all the experiments were continued through the night and the final results noted in the morning. A study of the curves showing the shrinkage and the fact that all pieces were bone dry in the morning tends to show that the pieces were dry before the time of final reading. Owing to the difficulties involved, no experiments have yet been run which would give the exact total time required. Even the 21 1/2 hours is about 1/3 the time required in ordinary practice.

I learned some time since that this method was in use in drying poplar, and that it was the only way in which that wood could be dried without cracking. This is in line with what Mr. Stover said on the subject.

It appears to me that this method would help in the drying of heavy china and porcelain, as its use tends to overcome the unequal heating and consequent unequal expansion and contraction of the ware, and causes the ware to dry more evenly. Let us hope that both Mr. Hope and Mr. Simcoe will add to the subject in question.

Mr. Ashley's suggestion, is I believe, correct, and care would be necessary in the aging of the clay to avoid the expansion cracks. Those tests were made with large blocks and the heating was rushed too rapidly, although

we only found a difference of 10 degrees between the outside and the center of the large blocks at the close of the steaming period, and this would not seem to be great enough to cause the cracking. As stated in the paper, the large blocks were made of a clay which is very difficult to dry in any manner.

THE EFFECT OF PRELIMINARY HEAT TREATMENT UPON CLAYS.*

BY

A. V. BLEININGER, Pittsburg, Pa.

This subject was brought to our attention by a practical problem which involved the use of a very plastic clay possessing a peculiar structure and known as joint clay. This material is glacial in its formation and while readily molded it cannot be dried economically owing to the great loss due to cracking. The cracks observed seem to indicate a somewhat cubical structure. These clays are exceedingly fine grained and the trouble experienced is evidently due to excessive plasticity. Long continued storing in the sun or weathering during winter seemed to overcome this difficulty. In our work the same result was obtained by drying the clay as it came from the bank before molding it, to a temperature of 200° C. when it seemed to lose its objectionable qualities, showed a greatly decreased drying shrinkage and gave but a small loss on drying the ware.

Owing to the lack of other clays the inability to work up this material has been a source of considerable loss to the brick manufacturers, especially since some of the joint clays burn to a very desirable color, show excellent strength and hold up well in the fire.

There is no practical objection to carrying out the preliminary drying in a rotary dryer since the cost of this process is not prohibitive in many instances though, of course, it would be advisable wherever possible to make use of the natural weathering and freezing, either by winning the material in the fall and exposing it to the weather

* By permission of the Director, United States Geological Survey.

in heaps or by plowing trenches into the shallow clay deposit and thus permit of this action without digging.

Other industries, such as the manufacture of roofing tile, terra cotta, etc., might find it advantageous to use the rotary dryer in order to improve the working quality of highly plastic clays, reducing the drying shrinkage, warping and drying loss.

In this connection, however, we must understand clearly that clays deficient in plasticity are injured by this treatment since they lose part of the plastic character and bonding power.

There are many clays which cause drying troubles owing to their excessively plastic, fine-grained structure in which the water has great difficulty in passing to the surface of the ware, so that the rate of evaporation on the outside is far in excess of the rate of flow from the interior. In many cases simple dilution with sand is sufficient to equalize the distribution of water; in others, this procedure fails, as in the case of the joint clay. It may be, however, that by pugging the sand into the clay with extreme thoroughness the difficulty might be overcome in all cases. Usually, the preparation is far from being sufficient since these clays coming from the bank in the wet condition are not readily worked by the machines generally employed and it would be necessary to resort to the use of the wet pan.

We have no reason for assuming that the preliminary drying treatment brings about a permanent destruction of part of the plasticity, and there is little doubt but that such a dried clay when exposed to the weather in the moist state would again resume its original plastic character. This resumption, however, requires a certain amount of time which is not allowed it in the usual process of manufacture. Hence, by making use of this lag we obtain the benefit of reduced plasticity. We should expect clays to differ in this respect. Some of them undoubtedly show considerable lag and hence preliminary drying could be

used to advantage, while others would exhibit such a short lag that they would resume their full plasticity in the ordinary course of preparation and drying.

As to the actual change brought about by the preliminary drying we must have recourse to analogous cases. If clays are collodial, as we have every reason to believe, they ought to follow the behavior of colloids in a general way. Fortunately, some work along this line has been carried on with pure colloids such as aluminum hydroxide, ferric hydroxide, and silicic acid. For instance, it is a well known fact in the laboratory that such gelatinous precipitates as aluminum hydroxide when dried on the filter are much easier to wash free from salts than in the wet condition. A pottery body after being made up into ware and dried in the usual steam dryer and again made plastic is found to be somewhat deficient in working quality and hence such waste is used for casting.

J. M. Van Bemmelen (*) in dealing with pure silicic acid assumes this substance to possess a structure which represents a more or less advanced transition stage between a solid and a liquid and hence encloses a certain amount of liquid. The colloid does not form a chemical compound with the liquid but the case is one of absorption. The liquid between the pores of this cellular structure leaves at first at a rate corresponding to the evaporation of water, in the case of silicic acid this holds true for a water content of from 120 to 25 molecules. Below this point the liquid between the pores leaves at a continually slower rate owing to the narrowing of the capillaries. Also the vapor tension of the colloid decreases constantly corresponding to the decrease in the content of absorbed liquid. At the same time constant changes occur in the physical condition of the substance which are slow at ordinary but accelerated at higher temperatures.

Van Bemmelen studied the inversion points by placing the silicic acid gels into dessicators containing 36 con-

*Zeitschrift für anorganische Chemie 18. 14—36, 18. 98—146. 20, 185—211.

centrations of sulphuric acid and hence corresponding to 36 aqueous tensions. He found several inversion points in the resulting dehydration curve. First, the substance becomes dull and fluorescent, then white like porcelain and finally opaque white, like chalk without gloss. This inversion changes the dehydration curve since for a distance it runs parallel to the abscissa. The capacity to hold water then decreases more rapidly than before the inversion point. On continuing the dehydration still further the dimness disappears just as it appeared. The gel becomes porcelain-like, of bluish fluorescence and finally as clear as glass, remaining thus until the final dehydration. Also, when the gel is at once exposed to higher aqueous tensions, after the inversion the gel becomes gradually homogeneous and clear as glass. These inversions may be repeated and they are hence reversible under certain conditions. It is evident, therefore, that certain changes occur in the micellian structure of the colloid at these inversion points, forming new coagulations which disturb the continuity of the dehydration curve.

By taking now the silicic acid pats which had been carried on to the lowest aqueous tension (most concentrated sulphuric acid) and placing them in the dessicators containing the more dilute sulphuric acid solutions, rehydration takes place. Plotting again the molecules of water at each stage against the aqueous tension, it was found that the first dehydration curve was not reproduced but that a distinct lag was observed corresponding to the hysteresis of the magnetization curve for iron. In other words, while a certain aqueous tension in the case of the fresh silicic acid corresponded to a certain amount of water, the same tension in the rehydrated substance was equivalent to a smaller amount of water.

We observe thus a strong similarity between the silicic acid, one of the best-known colloids, and clay.

For the purpose of investigating the behavior of clays it was decided to select seven plastic clays of which two

had given trouble in drying to such an extent that their use had to be practically abandoned by manufacturers. The other clays were taken because they simply represented types of plastic materials.

No. 1. Exceedingly plastic clay from Ft. Pierre, North Dakota, (Through the kindness of Prof. Orton). This clay was exceedingly difficult to dry.

No. 2. Fire clay from St. Louis, Missouri.

No. 3. Tennessee ball clay No. 3.

No. 4. New Jersey sagger clay—J. Prall, Woodbridge, N. J.

No. 5. Pike No. 20, English ball clay.

No. 6. Texas Lone Star kaolin.

No. 7. Minnesota joint clay, Albert Lea, Minn. This clay is causing great loss in drying drain tiles and brick.

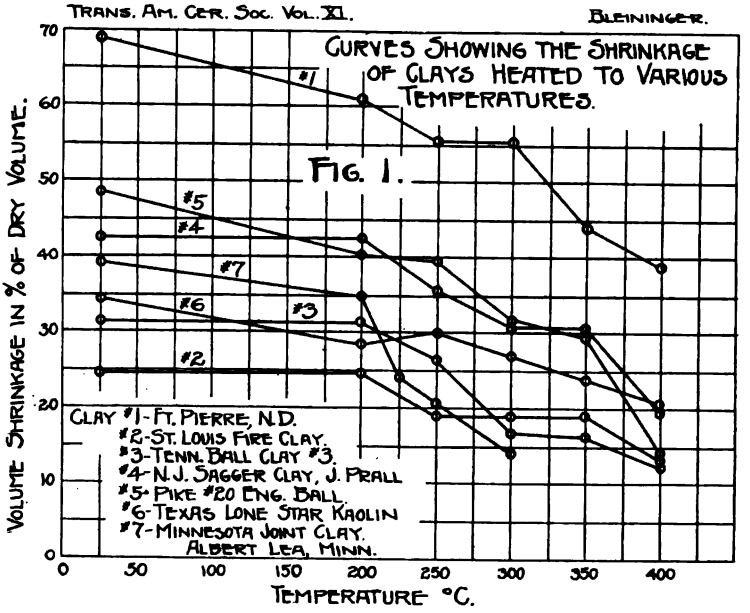
It is evident that the simplest and best method of following the behavior of these clays in drying is the determination of the volume shrinkage. Although in this work it is proposed to study the porosity of the clays thus treated, determined from the real and apparent specific gravities, the exterior volume changes must, in the nature of the case, remain the most important criteria of the behavior of the clays. Each of the seven clays was thus made up into a pat of about 400 grams, by adding sufficient water to convert it into a soft plastic mass and working it thoroughly. In order to reach a state of equilibrium and to allow sufficient time for the development of plasticity, the seven pats were allowed to remain in a dessicator over water, for one week. Then after thoroughly working the clay by hand from each pat there were made six smaller pats weighing about 50—60 grams. One pat of each clay was made into a bricklet about 35 grams in weight, the volume of which was determined at once by soaking in petroleum for some time, then placing it into a Kjeldahl flask and measuring the volume of petroleum displaced by means of a burette reading easily to 0.05 cc. The experimental error in the measurement of the volume by many

trials was not found to exceed ±0.1%. These seven bricklets (one from each clay) were then dried to constant weights in a water-jacketed copper drying oven at 85°—90°C. When dry they were immersed in melted paraffine for some time, which was allowed to drip off, and when cool they were placed in petroleum. After about an hour their volumes were determined as before. The amount of water necessary to make the clays into a plastic mass was gauged entirely by the judgment of the operator and this was found to be as accurate as any other possible means.

The remaining five pats of each clay were heated to five temperatures (one for each temperature) in a round, heavy drying oven, provided with an air jacket and with three tubulatures. A thermometer was inserted into the middle opening. The temperatures selected were 200, 250, 300, 350 and 400 degrees C. After reaching the desired temperature the heat was held there for three hours. After this drying treatment the pats were crushed in a porcelain mortar, passed through a 20-mesh sieve and made up with water into bricklets of a soft consistency weighing about 35 grams. These were allowed to remain in a dessicator over water for 16 hours so as to allow time for the development of plasticity and yet not too long so as to bring out the lag in the volume change. After removing from the dessicator the volumes of the bricklets were determined as described above and they were placed in the water jacketed drying oven at 85°—90° C., where they remained until constant in weight when their volumes were again ascertained.

In Fig. 1 the volume shrinkages of the clays expressed in terms of the dry volume have been plotted for the six temperatures and it is observed that no significant changes occur until 200° C. is reached when all clays excepting No. 6 show a decided drop. The clays differ however as regards working quality after being heated to 200°. The Ft. Pierre clay has not yet lost its excessive plasticity at 200° and does not become granular in its appearance until

300° has been reached. At this temperature a distinct coagulation takes place and the clay appears to have changed in its entire physical behavior. It is molded far more easily and dries without difficulty as far as could be told from the small bricklets made. There was not sufficient clay at hand for making larger pieces.

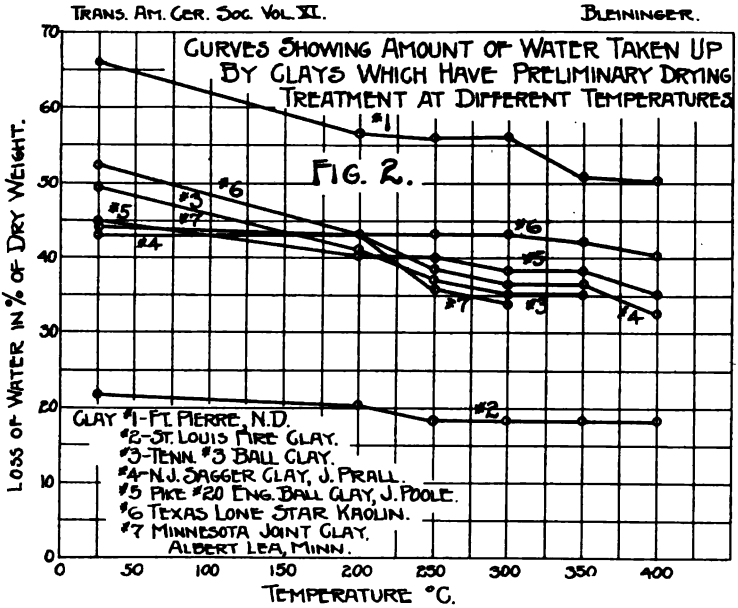


The St. Louis fire clay did not show a decided change in its properties below 250° and the total effect was less marked in this material than in others, since it did not possess excessive plasticity.

The Tennessee ball clay did not appear to be changed up to 300° when it had lost a great deal of its plasticity and had become "granular" in appearance. The same was practically true of the New Jersey sagger clay and the English ball clay, although the latter was more sensitive to heating at 200° and had suffered an appreciable loss in plasticity at that temperature.

The Texas kaolin was remarkably resistant to the heating treatment and did not show any decided change in its plasticity till a temperature of 400° had been reached.

Particular sensitiveness to this treatment was shown by the Minnesota joint clay which suffered a decided change in its character as was indicated by a change in color, the assumption of a granular appearance and de-

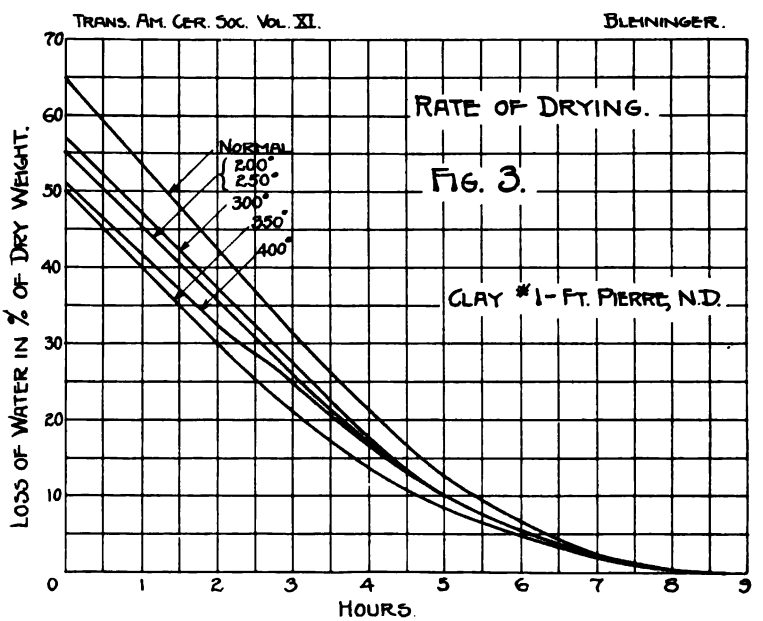


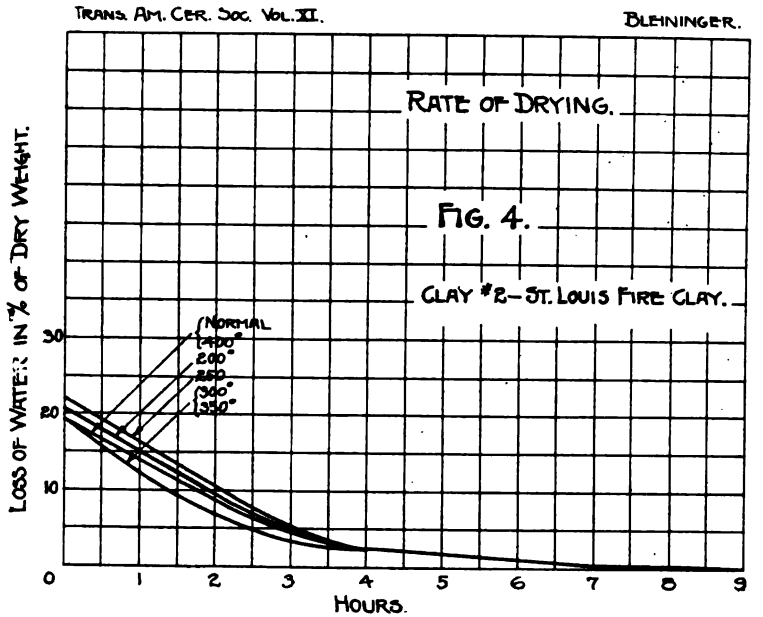
crease in plasticity at 200°—225°. In this condition it was dried without any difficulty and worked well in moulding.

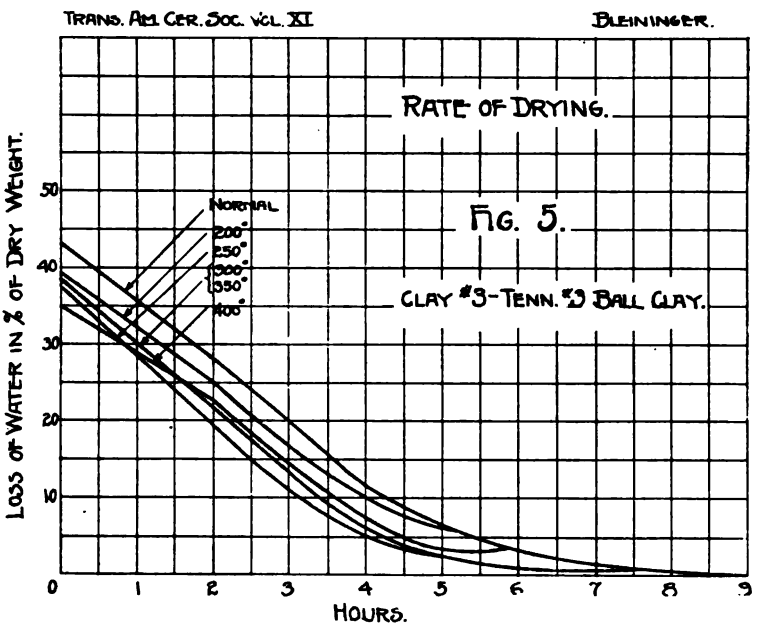
In each case after heating, the amount of water required in making up these clays to a plastic mass was decreased considerably as is shown by the curves of Fig. 2. However, no direct relation seems to exist between the drop in the volume shrinkage and the amount of water required. This seems to indicate that we are dealing not

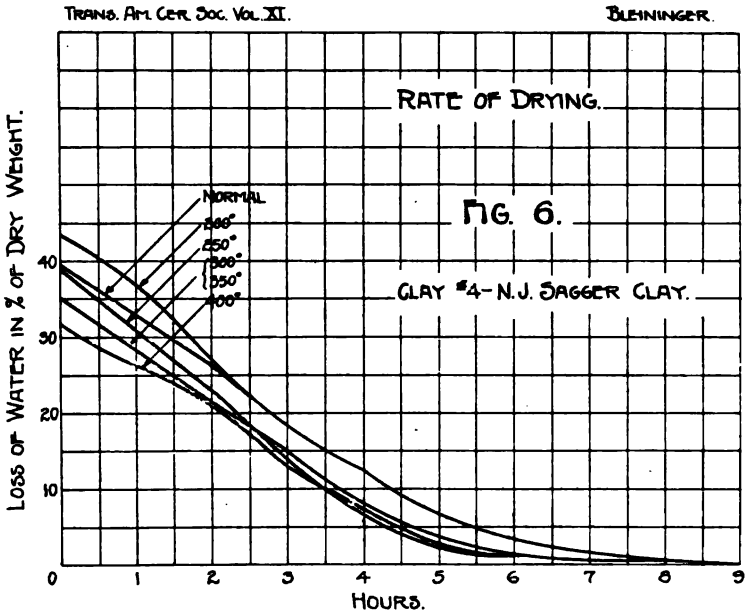
merely with a decreased capacity for water but also with a change in the entire physical structure of the clays.

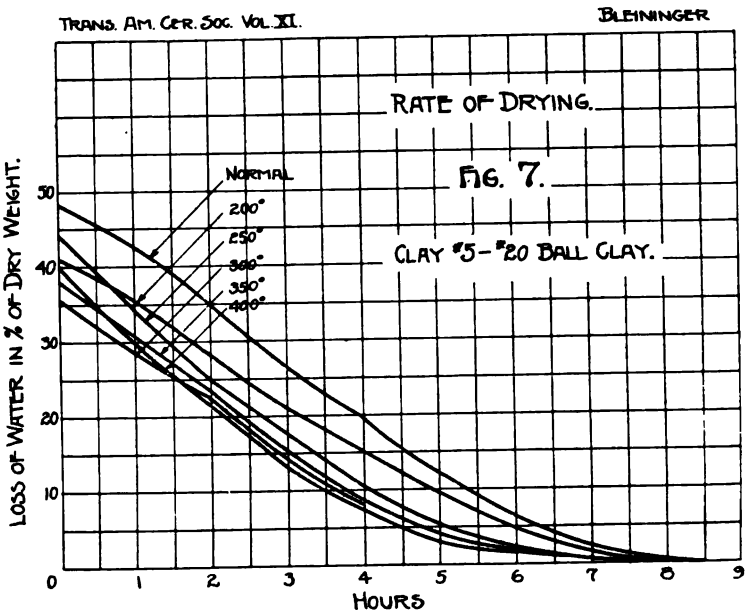
In order to determine the rate at which the drying takes place in the case of the different clays heated to the different temperatures, 36 small cylinders were made of six clays, corresponding to the five temperatures and the clays in their normal state. These were molded in the same mold and were placed into a water-jacketed drying oven kept at a constant temperature of 60° C. These cylinders were weighed every hour. The losses of water in per cent were then calculated and plotted as shown in Fig. ures 3, 4, 5, 6, 7 and 8. From these curves we observe that the rate of drying is not increased by the heating treatment and remains practically the same as for the normal clay. Taking into account the lower amounts of water in the dried clays the rate of loss is evidently the rate of evaporation under the constant conditions of the drying oven.

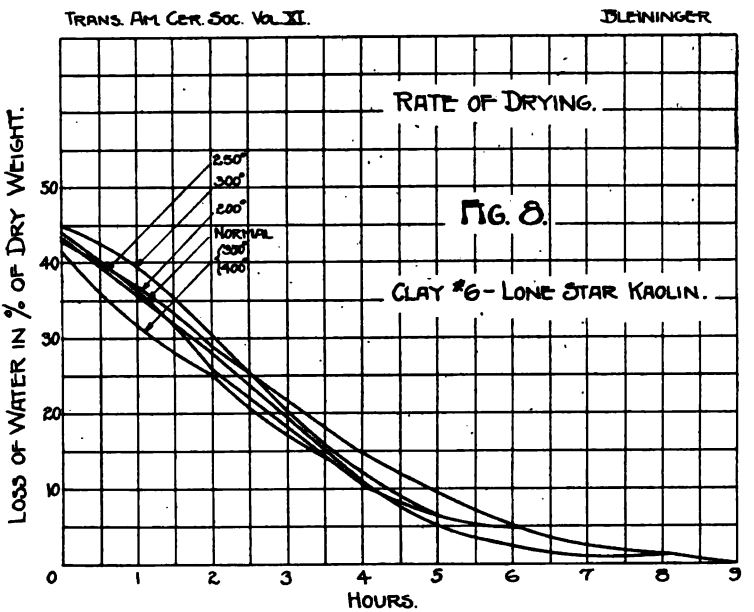



TRANS. AM. CER. SOC. VOL. XI.
BLEININGER.
RATE OF DRYING.
FIG. 4.
CLAY #2—ST. LOUIS FIRE CLAY.
LOSS OF WATER IN % OF DRY WEIGHT.
NORMAL
400°
200°
250°
300°
350°
0
10
20
30
1
2
3
4
5
6
7
8
9
HOURS.


TRANS. AM. CER. SOC. VOL. XI
BLEININGER.
RATE OF DRYING.
FIG. 5.
CLAY #3—TENN. "D" BALL CLAY.
LOSS OF WATER IN % OF DRY WEIGHT.
NORMAL
200°
250°
300°
350°
400°
0
10
20
30
40
50
1
2
3
4
5
6
7
8
9
HOURS.


TRANS. AM. CER. SOC. VOL. XI.
BLEININGER.
RATE OF DRYING.
FIG. 6.
CLAY #4 - N.J. SAGGER CLAY.
NORMAL
200°
250°
300°
350°
400°
LOSS OF WATER IN % OF DRY WEIGHT.
HOURS.


TRANS. AM. CER. SOC. VOL. XI.
BLEININGER
RATE OF DRYING.
FIG. 7.
CLAY #5 - #20 BALL CLAY.
NORMAL
200°
250°
300°
350°
400°
LOSS OF WATER IN % OF DRY WEIGHT.
HOURS



CONCLUSIONS.

1. The loss in plasticity suffered by clays at increasing temperatures is not abrupt but gradual. In the time allowed the clays examined in this work (16 hours) for the resumption of plasticity the original condition was only partially recovered, resulting in decreased shrinkage under practical conditions of working.

2. The decrease in shrinkage went hand in hand with a decrease in the amount of water required to make the clay into a plastic mass but no simple mathematical relation existed between the two factors.

3. As the shrinkage decreased the clays became "shorter" and appeared to become granular. Some of the clays changed in color, appearing to become darker and reddish.

4. The rate of drying of the dried clays did not differ materially from the rate for the undried clays.

5. It does not follow that the more plastic a clay is originally the more it is affected by the heating treatment. (Texas clay). Clays of lower plasticity may be rendered still less plastic but not at the same rate as highly plastic ones.

6. The temperatures at which these changes take place may vary from 200° to 350° C. for different clays, although the latter temperature is probably the limit for most clays as far as practical considerations are concerned. Further decrease in plasticity is not usually desirable. Each clay therefore seems to have its own practical inversion temperature.

7. If exposed to the action of water for longer periods it is very probable that the clays would resume their original plasticity. However, in the time usually allowed in working clays the slowness or the "lag" in the resumption of the plasticity may be used to good advantage in dealing with exceedingly plastic clays or in manufacturing such products as roofing tiles, terra cotta, etc.

All of the clays tested to 250° and above caused no difficulty in drying and showed no cracking.

In carrying out this work the thanks of the writer are due to Mr. G. H. Brown of the U. S. Geological Survey, for the care and attention given to the experiments and measurements involved in the investigation.

DISCUSSION.

Mr. Purdy: Those who have "rubber" clays will be interested in discussing this paper. I know W. D. Gates is interested in this subject.

Mr. Gates: I am very much interested, but absolutely as a learner. I was very much interested in the experiments described in this paper for they seem to bear out some experiences of my own, some difficulties I had; but I do not think I can throw any light on the subject. I have found clays which would look exactly alike, one of which would dry without cracking and the other would be noth-

ing but cracks. That is how they came to be called "rubber" clays. The only difference I could see was that one was possibly a little darker shade than the other. Then when the clays were mixed up in a thick slip a difference could be noticed in the fact that when gathered on the slab and swept up in pyramid form by the hand, the good clay would retain its position while the other would flow off in the manner of quicksand. The difficulty led to our having to give up the use of some clays. I am rather inclined to think that this heat treatment might have benefited those clays, and I intend to do some experimenting. This recalls to my mind an incident which goes to show how we work in the dark. For convenience in handling, we constructed a drier, the clay being brought in and thrown on hot steam pipes, so we did this same thing without intending to. I remember, since talking with the author of this paper, that we secured good drying results from these clays. I am very glad, indeed, that Professor Bleininger has undertaken this investigation.

Mr. Campbell: I would like to corroborate what Mr. Bleininger has said in regard to reducing cracking by this preliminary heat treatment. Last summer I was testing out three clays and did this very thing. A clay that would crack without this preliminary heat treatment, I found would come out perfectly smooth, without cracks or fractures, if first given this treatment.

Mr. Kerr: In regard to the curve shown here, as I understand it, it is the actual volume shrinkage and not the apparent volume shrinkage?

Mr. Bleininger: The actual cubical shrinkage.

Mr. Purdy: The exterior cubical shrinkage?

Mr. Bleininger: Yes, sir; exterior, not the absolute.

Mr. Purdy: Have you made any observations of the clay particles themselves?

Mr. Bleininger: Not yet: the experiments were begun a little over three weeks ago. They are under way now, but of course we have not done many things we would like to have done.

Mr. Purdy: No doubt. The question is as to measurements of the clay particles themselves.

CRAZING AND SHIVERING.

DISCUSSION OF MR. GRIFFEN'S ARTICLE, IN TRANS. VOL. II.
PROPOSED BY

JOHN SANT, East Liverpool, Ohio.

Mr. Sant, after reading Mr. Griffen's paper:

I don't know that it is proper for me to criticise this paper, as the author is not present. His views are much at variance with those generally accepted, but so far as I can learn, his paper has never been discussed at our meetings or in our Transactions.

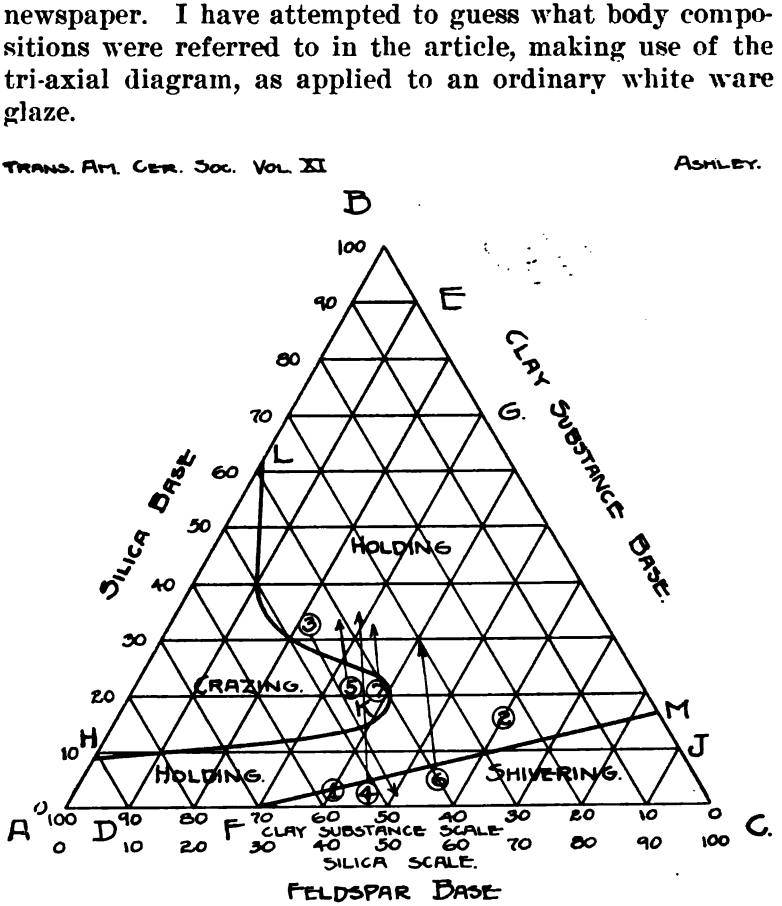
Mr. Watts: I would say that Mr. Griffen has retracted his statements, or rather changed his opinions, but inasmuch as he has not gone on record as contradicting these statements, I think it is proper to discuss them and to show wherein he is in error.

Mr. Sant: I have always held the view that shivering was invariably caused by a defect in the body, which defect is brought out by the glazing. To remedy shivering you should never proceed to change your glaze formula, but your body formula. I have introduced this matter not to give information, but to get some. I have for a long time inquired into this matter and have not been able to get all the information I wanted; I felt if it was to be had anywhere, it should be here.

Mr. Ashley: I have discussed crazing and shivering once or twice previously.* The matter in these discussions covers pretty thoroughly cases similar to those presented by Mr. Griffen. It has seemed to me that Mr. Griffen's paper is too indefinite. He gives altogether no idea of the compositions of the bodies and glazes he is talking about.

*Trans. VII., 69—78, 89—94, IX., 59.
Brick 23, 81 (1905).

A discussion of such a paper could not reasonably be expected without more definite statement of cases. As presented, the article resembles the puzzle column of a weekly newspaper. I have attempted to guess what body compositions were referred to in the article, making use of the tri-axial diagram, as applied to an ordinary white ware glaze.



In Fig. 1, let the point A represent 100 per cent of clay substance, any point on the line BC zero per cent clay substance, and any intermediate point a percentage proportional to its distance from line BC to the point A. Similarly, let point B represent 100 per cent feldspar, the line AC zero per cent feldspar, and intermediate point

intermediate percentages. Also, let point C represent 100 per cent silica, any point on the line AB zero per cent silica, and any other point an amount proportional to its distance from AB toward C. For example; any point on the line DE represents 10 per cent silica, any point on the line FG 30 per cent silica, any point on the line HJ 10 per cent feldspar. The point (1) is at 2 per cent feldspar, 40 per cent silica, 59 per cent clay substance. Every possible mixture of clay substance, feldspar, and silica is represented by a point on this diagram. All points in the area HKL represent bodies on which a whiteware glaze is likely to craze, points in the area FMG bodies on which it will likely shiver. On other bodies it will usually hold.

Griffen's case 1 may possibly occur on a body having the composition given by point (1). Suppose his clays contained considerable soluble salts. These would come to the surface in drying. Then if the glaze were dipped thin, enough bases from the soluble salts might be introduced into the glaze to make it decidedly more basic. Increasing the basicity of a glaze makes it more liable to craze. If the glaze were dipped thicker, the soluble salts from the surface of the clay would form a smaller percentage of the total glaze, so that the effect of increasing thickness of glaze would be increased acidity, and this may be carried far enough to give shivering.

Case 2, the same glaze on another body, which we will assume to be of highly silicious composition, as given by point (2). An ordinary glaze feeds on such a body, becoming more acid. The thicker it is applied the less alteration of composition will be effected, and consequently the more likely it will be to craze.

Case 3 is illustrated by point (3). "Repeated additions of a silicious clay, to a vitrifying clay, caused it to pass from standing to crazing, then to standing, then to shivering, glaze and heat being the same throughout."

Case 4, point (4). "The repeated additions of feldspar to a shivering clay caused it to pass from shivering

to standing, then to crazing, then to standing, glaze and heat being the same throughout."

Case 5. "Increasing the biscuit heat given a body caused it (a) to pass from shivering to standing, (b) then to crazing, (c) then to standing, glaze and gloss heat being the same throughout." I have found instances of each of these steps but never all combined. The case is the same as case 4 in its steps, and its reason may be similar, namely that as the temperature increases more flux (assume coarsely ground feldspar) becomes active.

Case 6. "My constant practice, in order to stop either shivering (see point (6)), or crazing (see point (5)) in a vitrified body, when I wish it to remain a vitrified body, is to add spar to it." As in some cases the holding area between crazing and shivering is very narrow, points (5) and (6), case 6, may in reality be quite close together. Weelans found it so* at cone 14 with a glaze of the formula 0.117 ZnO, 0.313 K_2O, 0.570 CaO, 0.43 Al_2O_3, 2.98 SiO_2.

Case 7, point (7). "Either flint or spar added to an open body, upon which the glaze crazes, will stop the crazing."

As the region around K will be either open or vitreous according to the cone fired to, I feel justified in putting both cases 6 and 7 on the same diagram.

I trust these remarks will supply a handle to make Mr. Griffen's paper more manageable.

*Trans. VII., 73.

THE FLOW OF PLASTIC CLAY THROUGH DIES.

BY

WILLIAM HENRY ARTZ, Dayton, Ohio.

An experimental research on the subject in hand must be accepted with the following qualifications:

1st. The results are entirely consistent and in accordance with the peculiarities and properties of the specific clays under test.

2nd. The physical behavior of each individual clay is a problem in itself.

3rd. After obtaining good results the factors employed in such successful manipulation must be kept fairly constant or the quality of the clay column suffers in consequence.

4th. Like mechanical equipment may or may not give good results on two or more seemingly similar clays.

5th. No definite laws can at present be deduced from the behavior of the clays experimented with that would be entirely applicable to others, even of the same type.

6th. A careful study of the cases here encountered will, by deductive reasoning, aid the investigator in facilitating his experiments and arriving at the proper conditions for successful manipulation of other clays without a long series of intermediate trials and the incurrent expenditure of time and money.

STATEMENT OF CONDITIONS.

There are three important factors to be considered from the standpoint of a practical ceramist before a clay can be recommended for the successful and economical production of commercial wares. These factors are, briefly speaking, the forming, the drying and the burning of the

product. Evidently the failure of the clay to behave satisfactorily during any one of these stages of manufacture would eliminate it from the field of workable clays.

The experienced investigator can give more or less plausible reasons for the behavior of a clay in drying and burning, although each clay is in itself a problem for experiment and study. But in forming plastic clay wares by means of forced flow through dies the difficulties encountered in obtaining good results are less definitely accounted for than are imperfect drying or burning results. The nature of the imperfections, if any, in a column of clay flowing from a die is always evident, but the cause of such is generally difficult to remedy even if the seat of the trouble is definitely located. In the majority of cases satisfactory results can be obtained if extensive enough experiments are made to determine the proper mechanical equipment, suitable lubrication and a correct preparation (tempering) of the clay. The last of these three factors demands less attention, or rather admits of greater variation than the two former ones.

The work here undertaken deals with the formation of a continuous clay column which must subsequently be cut transversely at the desired intervals to produce the individual pieces of ware. The formation of a clay column by piston or plunger machines will not be considered. The items—mechanical equipment, including the means of forcing the clay through the die, the die itself and the lubricating substance, with the method of applying same—comprise the major considerations of this work.

No attempt will be made to discuss any of the various theories of plasticity which have been brought forth from time to time. Such discussion would prove of no value to the practical clay worker and hence the theoretical phase will be eliminated as far as possible, dwelling upon the results of the phenomenon of plasticity rather than its causes.

Plasticity involves two ideas:

1st. The particles of a mass must be mobile; that is they must be able to move on each other.

2nd. The internal cohesion of the mass must be sufficient to hold the particles still, except when disturbed by a superior force.

All substances have more or less of this cohesion. The mass with mobile particles has the qualities between a solid and a liquid. Plastic clay occupies a position between these two states of matter.

It is the nature of this plasticity and the texture and consistency of the plastic clay that play an important role in its flow through dies. Any clay may be made to flow through a die if a great enough pressure is applied, but the problem is to overcome the defects which make the column either imperfect as to structure or as to being in cross-section other than that of the die through which it passed. The essential requirements of the method are 1st, a reservoir of clay connecting to the die; 2nd, some means of applying pressure to the clay, and 3rd, a die consisting of a tube of the proper cross section.

The experiments that follow were made on an auger machine for that is the only way in use of forcing clay continuously through a die. A piston or plunger gives a connected clay column but, in the nature of the case, its operation is intermittent. The method of pressure application imparts its own peculiarities to the resultant column and hence the results of a study of one method would not be applicable directly to the other, and vice versa. Either method may be used in making wares of both solid and hollow type.

The Auger.

The flow of clay through a die is affected by certain forces which produce structure in the bar. The source of the pressure still further affects the structure. This structure is due to what is known as differential flow. The exterior of the bar, being in contact with the walls of the

die, is held back by it. The center being surrounded by moving material has less friction to endure, hence it moves faster. The result is a different rate of flow on the outside and middle of the bar and hence a tendency for the two portions to slip on each other and laminate. The revolving motion of the screw also develops a spiral structure and the clay is polished by contact with the smooth metal surface. These polished spots do not readily weld up again in some clays and the result is a line through the bar marked by laminations arranged spirally. The kind of auger, whether single or double thread, affects this greatly. The pressure is greater in the former hence the slick spots are more numerous and the spiral structure more developed. The bar consists of one spirally arranged stream of clay. But with the double thread auger each lip is discharging a bar so to speak, within the chamber of the machine, and these two bars blend and mingle together in the die. One breaks up the laminations of the other to a certain extent and there is a criss-cross lamination and a minimizing of the otherwise pronounced spiral structure of the bar.

It must not be understood that all clays worked with a single thread auger give perceptible marks of lamination, for that is far from the facts. Many clays can be worked equally well with either type of auger, for all clays do not laminate equally from auger treatment. It depends perceivably upon the capacity of the clay for taking polish. Therefore fine grained fat clays could be expected to laminate, while gritty, coarse grained, and little plastic clays would laminate very little. But experiments show that there are many exceptions to this rule and it is often the unlooked for which happens.

The problem of laminations in a clay is of secondary consideration in these experiments; it is a factor which does not ordinarily affect the bar as to shape or external quality, although a laminated ware would naturally be inferior in drying and burning properties and in strength. But the differential flow caused by the revolving of the

spiral auger is of consequence in some cases, aside from the possible structure of the clay bar. The auger is like any other screw revolving in a circular casing. Material progressing through the threads of the screw will be discharged from the lips in a circular ring. Now in the case of an auger forcing clay through a rectangular die opening, greater pressures are exerted alternately at the two sides of the opening. Consequently a zig-zag motion will be imparted to the clay column marring or breaking it when it leaves the confines of the die.

A double auger, discharging as it does, simultaneously at points diametrically opposite, overcomes largely this swaying motion of the clay column and the pushing effect of the screw is in result more nearly like that of a piston or plunger.

The position of the exit of the die with reference to its distance from the discharging end of the auger is a factor also to be considered. If enough space intervenes between the two the tendency of the flow is to equalize itself throughout the cross-section of the bar, neglecting the friction of the walls of the chamber and the die. If this space is too short the bar may leave the die with a zig-zag motion, cracking laterally or longitudinally as the case may be, on account of the unequal auger pressures. A specific illustration of this point comes up in one of the following experiments.

The Die.

The most elementary die is a tube with solid metal walls and no taper, no arrangements for lubrication or for equalizing pressures. But this form of a die gives trouble. Some steps must be taken to overcome as far as possible the differential flow which is the common characteristic of all clays. The remedy for this is to reduce the outside friction or increase the interior resistance. The method of attaining the former result is lubrication and the latter, interposition of other frictional surfaces.

Some clays flow in contact with metal with comparative ease. Others adhere to the surface so that it is impossible to force them through, still retaining the shape of the die. The vast majority of clays require lubrication, at least where the cross-section of the ware produced is very large. All of the experiments of this work were made on dies of rectangular shaped openings and solid cross-section of clay bar. Hence satisfactory lubrication of the corners was of vital importance.

The modes of application of lubricants are as follows:

a. Surrounding the bar with a film of the lubricant, i. e., lubricating the entire surface.

b. Lubricating the corners and protecting the rest of the surface from the lubricant, so as to reduce the friction at the corners more than elsewhere.

c. Lubricating the corners early and the rest of the bar late, so as to assist the corner flow.

Lubricating dies are constructed of segments within an outer casing and between which the lubricant is injected. These segments are usually lined with overlapping scales, the overlapping being in the direction of the flow. The lubricant is introduced behind the scales and comes out between them.

The second method of equalizing pressures is that of interposing new frictional surfaces. The idea of this method is the same as in lubrication, i. e., to hold back the sides and ease up the corners. This may be done by

a. Cutting out the corners.

b. Giving extra cross-section.

Cutting out the corners in the rear of the die allows more clay to enter there than can leave at the front end in a like time, hence a greater forcing pressure is exerted at the place of highest friction. Giving extra cross-section merely allows a greater area of clay at the entrance than at the exit of the die and the resulting increased pressure in the corners assists in overcoming the friction there, while the other parts of the bar will move along in unison

with the corners. In practice both methods of equalizing pressures are used conjointly with more satisfactory results than either one alone would give.

Lubricants.

The adoption of a substance or mixture of substances for lubricating a column of clay flowing through a die depends primarily, of course, upon its suitability for the duty imposed, and secondarily upon the lesser considerations of convenience and expense. In the majority of clay working plants steam is available and it is by far the most common lubricant used. Steam both heats the parts of a die and forms a moist film between the clay column and the die liners. As to which of these factors exerts the greater influence upon the smooth flow of the clay, it is a matter of conjecture. But the fact is that in the case of all lubricants, the clay flows on the film of lubricating substance rather than on the lining of the die directly, and the additional presence of heat seems to contribute to the desired result.

Water is also a common lubricating substance, but when water works successfully steam can generally be used also. If the clay must be worked rather soft, the additional water has a tendency to make the surface of the bar slimy and difficult to handle. The above condition is a minor one, however, as it should not occur in a well regulated die. But in using water care must be taken that its pressure is not great enough to agitate the clay particles on the surface of the column, i. e. cause soggy spots. In this point water differs to a great extent from steam. The water pressure must be sufficient to force it around the bar and this is more difficult to regulate than getting a film of moisture at that place by means of steam.

Oils, soap-water, chalk-water, etc., may be used in special cases where steam and water have been proven insufficient by experiment. But none of these are used commercially in but few places, as they are not as con-

venient or economic as steam or water. As they are liquids the comments upon water lubrication may be applied here.

It may seem out of place to mention dry dies under lubrication, but as plastic clay columns are also obtained through this type of die, they may be spoken of as unlubricated. One type of dry die depends upon steam for heating the metal lining, there being no connection between the steam chamber of the die and the clay column. Here the heat of the walls of the die has a tendency to vaporize the moisture in the clay and in reality form a vapor film between the clay and the die walls. At least the effect of the heat on the reduction of the frictional resistance may be studied without the influence of direct contact of the steam.

In making wares of small cross section or hollow blocks the strictly dry die is generally used, as the effect of the friction of the walls is transmitted quite equally through the cross section and the result is rather only greater power consumption in forcing the clay through the die than unequal flow of the clay particles. Clays which give great difficulty in working in side-cut brick dies with lubrication can often be manipulated well on an end cut dry die or in hollow ware shapes.

The Effect of Temper.

If a clay is too soft it develops a characteristic effect in flowing through even a good die, "roughing" or tearing back at the corners. Or the corners may become detached from the bar within the die by friction and remain there as an obstruction to the clay following, thus giving a column with the square corners entirely lacking. When the corners of a die become thus choked the tendency of the clay will be rather to flow around this clogged up material than to force it through the die with the center of the column. This is easily explainable since the clay takes the path of least resistance and this clay sticking in the corners increases the resistance at those points.

The point might be raised that incorrect die structure might cause this latter defect in the column but it is not always a logical one as could be seen by working the clay a trifle less soft. A harder consistency of the material, within limits of course, would perfect a greater bonding strength between the particles and result in pulling the corners along with the center of the column. This increased hardness would also give the clay entering the corners from the rear of the die, a higher pushing efficiency. When the clay is too hard it lacks plasticity and is too granular. If it is plastic enough it is still rather dry and a different type of defect is produced. The defect shows itself by cracks similar to those obtained in drying some clay wares. The particles have not welded well and upon leaving the die separation along these dry surfaces takes place. The exact form of these cracks is difficult to describe but they are easily recognized and they become more exaggerated in the dried product. This cracking is naturally greater at the corners of the bar but the interior structure is deteriorated by dry spots and minute cracks in all directions.

As stated in the early part of this work, the tempering of a clay admits of greater variation, as a rule, than the auger, die or lubrication, referring of course to a clay which requires a certain set of mechanical conditions. But for a clay which can be formed into a good bar by means of almost any type auger and through nearly any style of die, this comparative statement probably does not hold good.

EQUIPMENT AND GENERAL TREATMENT.

Six different clays were experimented with and they covered in a general way the types of those used in stiff mud manufacture. Attempts had been made previous to the author's trials to work two of them but without success, while the other four had never been tested or worked. In order to present the details of the experi-

ments in a systematical way an exact description of the pieces of apparatus used will be given before the tests themselves are taken up.

The Auger Machine.

The Auger Brick Machine used was rated at a capacity of from 2,000 to 4,000 standard size brick per hour. Further description or details of its construction are unnecessary as it had no peculiarities which would influence the behavior of the clay more than any other machine of its type.

The Knives, Auger Wing and Auger.

The knives were steel blades about 6 inches wide revolving in the chamber of the machine beneath the hopper. They were set in consecutive order around a hexagon forged steel shaft and each knife made a 90° angle with the one preceding it. As constructed they had sufficient "lead" or "pitch" to pass the clay from one to the other on its forced journey to the die.

The auger wing was in reality a curved blade which filled in the interval between the last knife and the auger itself. It carried the clay from that knife to the thread of the auger and imparted the first touch of spiral movement to the material. Both the auger wing and the knives were standard equipment and they were not varied during the tests.

Two types of augers, single and double thread, were used, a change from one to the other being made as occasion demanded. The properties of these augers have previously been discussed, hence only a description will be given here. The single thread auger, illustrated by Plate II, was a screw of one continuous thread extending from the auger wing in the rear to the discharging lip in front. The double thread auger had a second thread starting at about 270° from the beginning of the first thread and continuing between the turns of the first thread to its

discharging lip. Hence this latter auger had two discharging lips diametrically opposite and delivering the clay simultaneously from each. In short, the arrangement of the two threads was quite like that of any so called double thread screw. The double thread auger is illustrated by Plate III. Both augers converged cone shaped towards the discharge end to conform to the walls of the nozzle of the auger machine in which they revolved.

Dies.

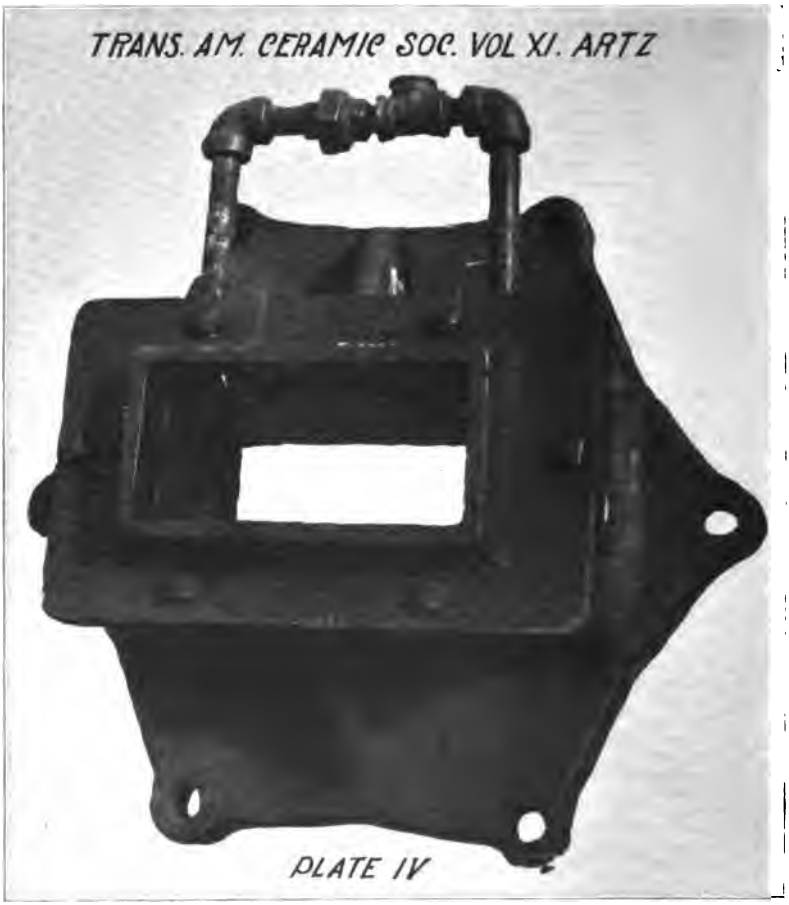
Two general types of dies were used, viz., end-cut and side-cut. The side-cut dies were of two classes, steam and water or liquid lubrication. The end-cut die was a dry die without an exterior heated chamber. The mode of applying the lubrication was that of lubricating the corners early and the rest of the bar late. The method of interposing new frictional surfaces was also a factor in the construction of the dies. In the lubricating dies the cross section of the rear of the dies was greater than that

of the dies, while in the dry die the rear corners were cut out bell shaped in the rear in order to allow the clay to have more pressure at those points than in the center of the column. In order to afford a thorough understanding of these dies and their working principles the construction details of each will be given.

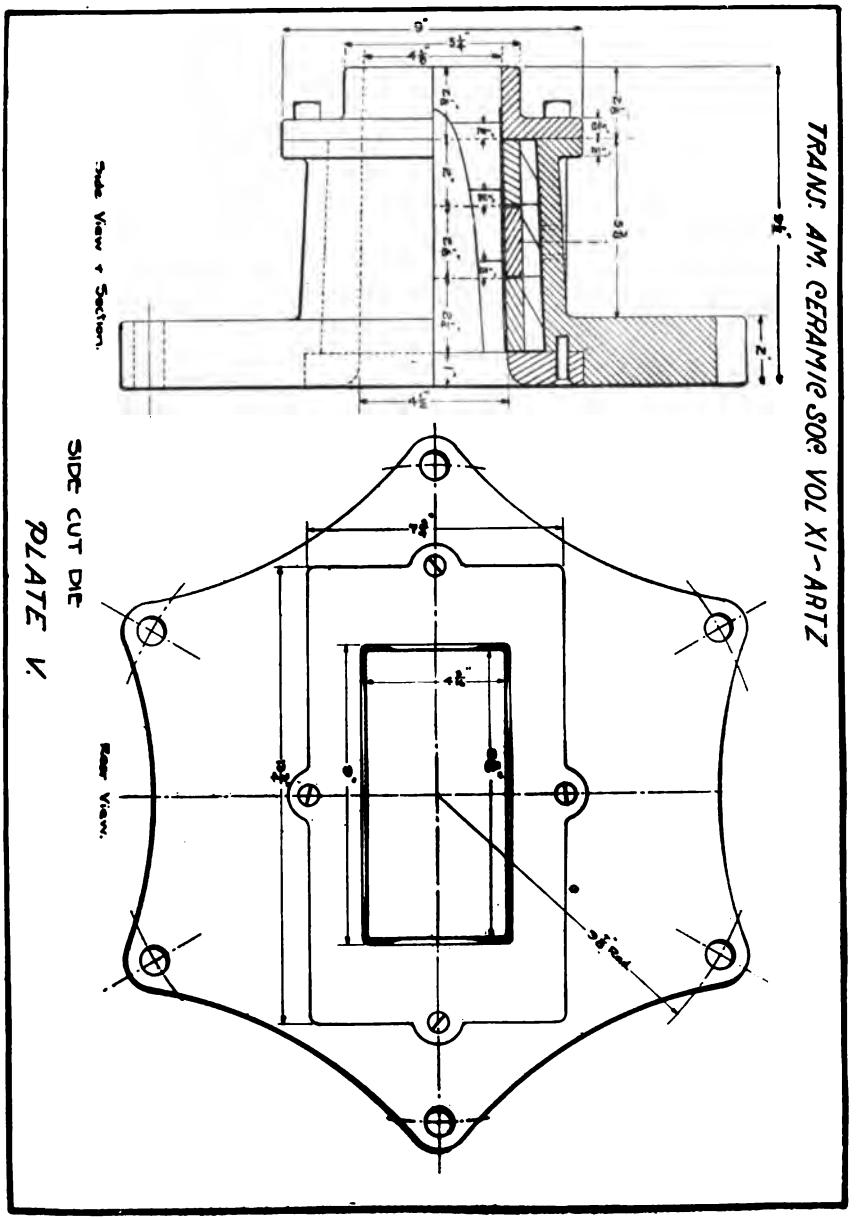
Die No. 1. A 4 3/16″ x 8 5/8″ side-cut, steam-lubricating, steel-lined die. The rear dimensions were 4 1/2″ x 9″ and the length was 9″. It consisted of five members, the housing, the cast iron liners, the steel liners, the slickers and the inlet and drain pipes. Plates IV and V show this die.

The housing was the cast iron casing into which the interior parts were fitted and by which the assembled die was bolted to the nozzle extension of the auger machine. This housing also acted as the action shell of the chamber in which the lubricant freely circulated around the iron liners within.

The cast iron liners were in the form of four rectangular rings each about 2 inches wide and $\frac{3}{8}$″ to $\frac{1}{2}$″ thick. They were held in position in the housing by projecting strips on each side. These units were not set together with a machine fit but enough opening was left between them to allow free passage of the lubricant from the chamber to the interior of the die. The front area of each rectangular ring was slightly smaller than the rear area of the same ring and a longitudinal cross-section of the interior surface of these pieces would appear thus:



Each of the cast iron liners was covered with sheet steel liners conforming exactly to their rectangular shape. These sheet steel pieces were crimped over the rear edge of the cast iron liners to prevent their movement by the clay pressures. Each one also lapped a trifle over the one in front of it and between the cast iron liners and between the lap of the steel liners the lubricant oozed from the chamber to the interior of the die. A gasketed


TRANS. AM. CERAMIC SOC. VOL XI-ARTZ
Side View & Section.
Rear View.
SIDE CUT DIE
PLATE V.

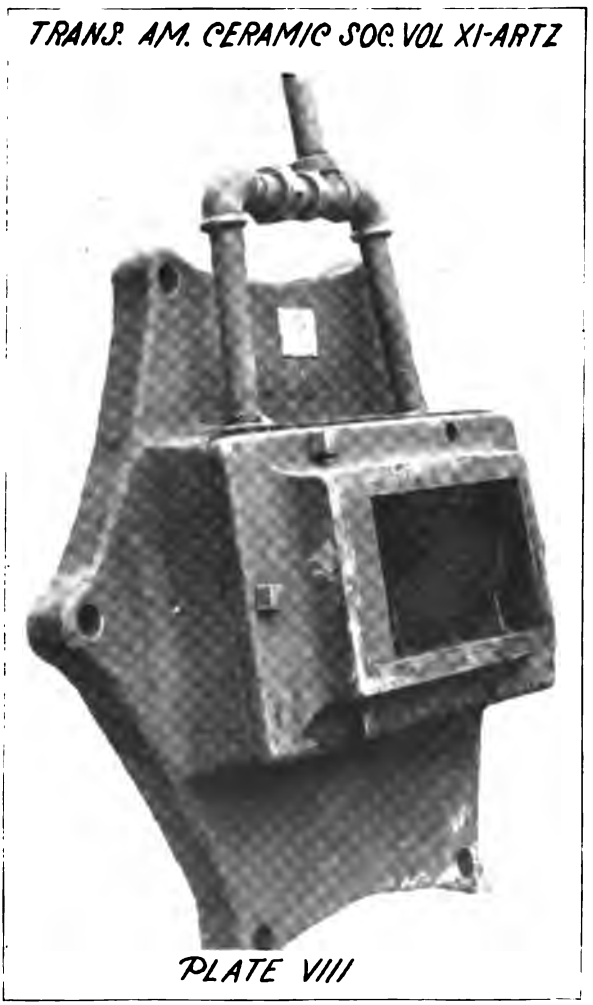
iron plate at the rear and front of the housing closed the chamber and prevented any leakage of the lubricant except as provided for between the scale like steel liners. If the die were used as now constructed the entire perimeter of each rectangular ring would be lubricated equally and no account would be taken of the greater friction in the corners. To care for this circumstance a means of lubricating the corners early and the rest of the bar late was taken advantage of. So here entered the so-called "aprons."

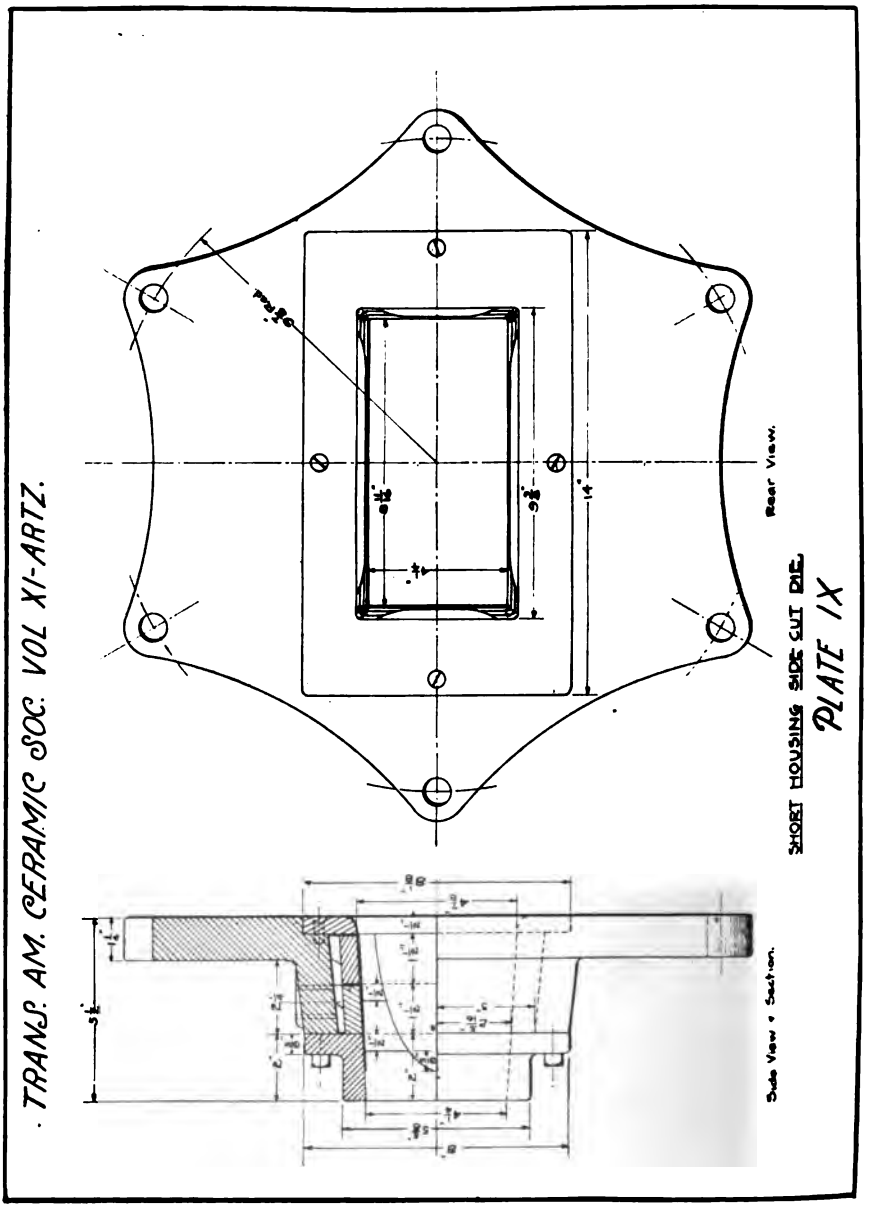
These were parabolic shaped pieces of this sheet steel fastened in by the rear cast iron plate. The sides, top and bottom of the die were each fitted with one of these "aprons" which extended to the front a sufficient distance to overlap the rear of the last liner in that direction. The lubricant coming through between the liners could not come in contact with the clay column except at the corners in the rear and thus the points of greatest natural friction were favored by the lubricant concentration brought about by these contrivances. As the clay traveled forward the areas of the "aprons" became less until at the exit of the die the entire surface of the bar was receiving lubrication equally.

The inlet pipe at the top of the die and the drain pipe at the bottom were merely the means of supplying the lubricant and of draining the die. Each pipe was fitted with a valve for regulating the flow of steam. During operation the upper one was regulated as occasion demanded while the lower one was kept almost closed, most of the steam entering the chamber being used in lubricat ing the column.

Die No. 2. A 4″ x 8 3/8″ side-cut, water-lubricated, steel-lined die. The rear dimensions were 4 3/4″ x 9″ and the length was 9 1/2″. In general its construction conformed closely to that of Die No. 1. But as the flowing quality of a liquid such as water is somewhat less energetic than that of steam, a means was provided to facili-

tate the passage of the lubricant from the chamber to the clay column. This was made possible by a series of small holes drilled in each cast iron liner through which the lubricant might pass in addition to the openings between them. After coming through the cast iron liners the distribution by the steel liners and "aprons" was the same as with Die No. 1.




TRANS. AM. CERAMIC SOC. VOL XI-ARTZ.
Rear View.
Side View & Section.
SHORT HOUSING SIDE CUT DIE.
PLATE IX

Die No. 3. A 4 1/4″ x 8 11/16″ side cut, steam-lubricated, steel-lined die. The rear dimensions were 5″x9 1/4″ and the length was 5 1/2″. On account of this last dimension the die is spoken of as a short die and is used on a clay of such a nature that it (the clay) will not flow successfully through a die of greater length and consequent larger amount of friction. Plates VIII and IX illustrate Die No. 3. Except that this die contained three liners instead of four, its construction is identical with that of Die No. 1.

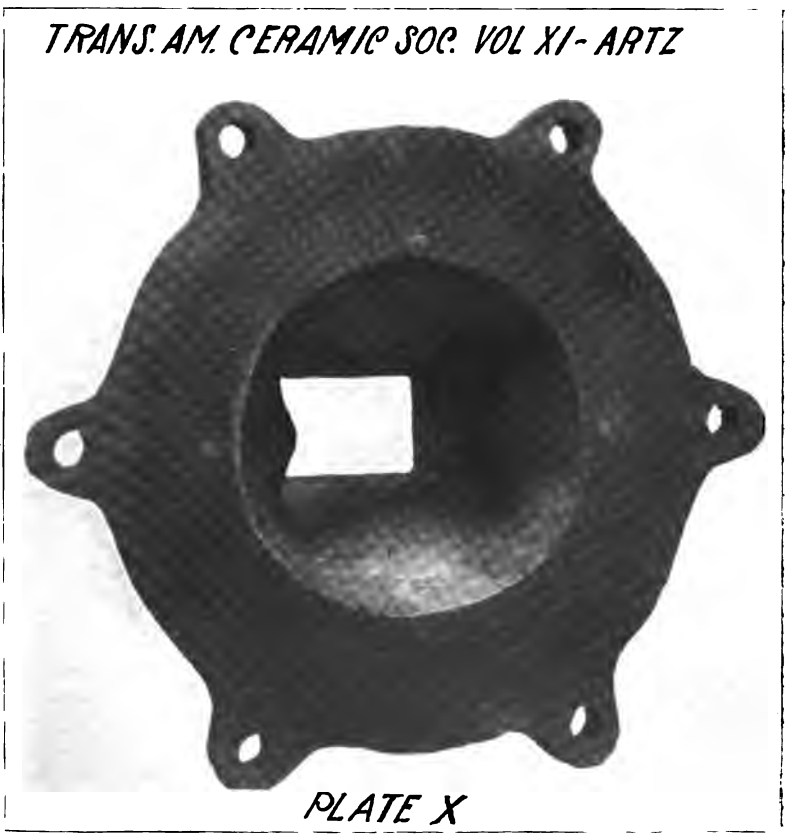
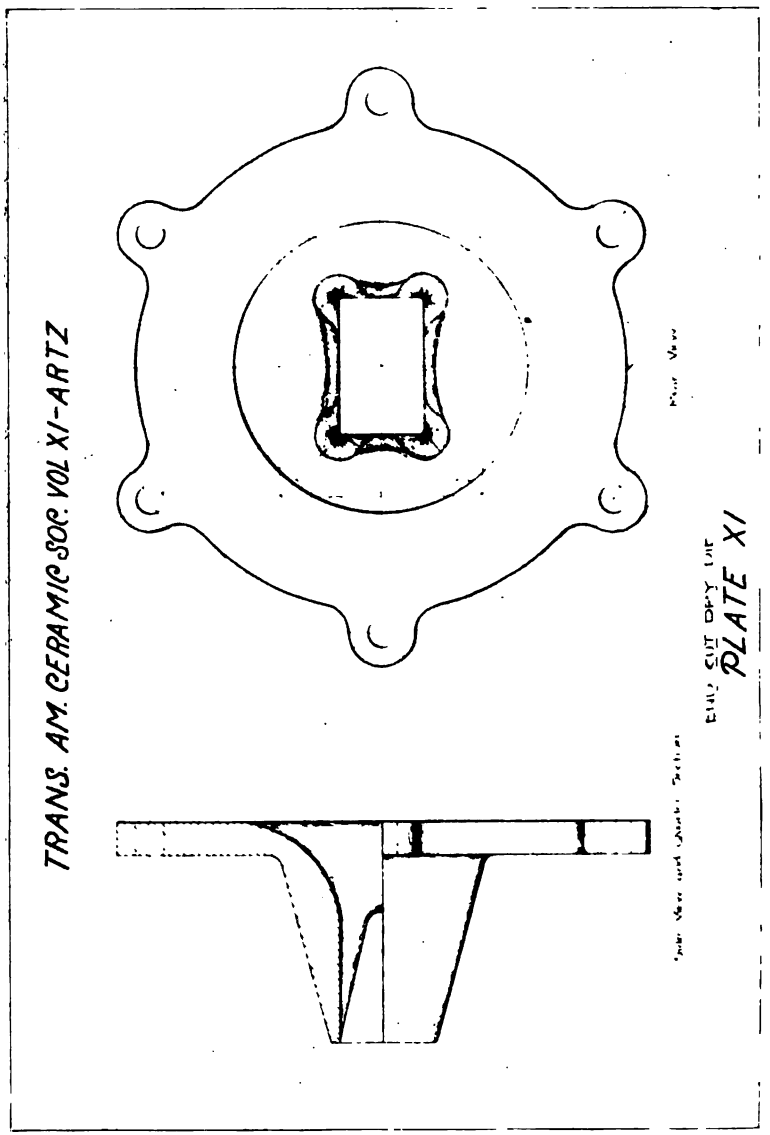


PLATE X


TRANS. AM. CERAMIC SOC. VOL XI-ARTZ
PLATE XI

Die No. 4. A 2 1/8″x4 1/4″ end-cut dry die, 6 3/4″ long of which Plates X and XI are photographs. This die was complete in one casting and cutting out the rear corners was the expedient used in equalizing pressures. The easy curves of the bell-shaped corners allowed the clay to flow easily into the die and in sufficient amount to exert the greatest forcing pressure at the points of highest friction. The photograph of this die portrays its construction better than words can describe.

Die No. 5. A 4 1/4″x9 3/4″ side-cut, steam-lubricated steel-lined, paving block die. The rear dimensions were 4 1/2″x10″ and the length was 9 1/2″. This die was similar to Die No. 1 in all respects except size. Its working principles were the same as that die and it could be expected to give similar results on a clay as would Die No. 1.

Tempering.

The clays tested in these experiments were given the best possible preparatory treatment and care was taken to work them at their best consistency and condition. Data on the water content of the clays as worked can scarcely be of much value in connection with the study in hand, as the proper temper is not judged by the amount of water added, but by a first knowledge of the case by examination. Still as a possible source of information and comparison, a determination of the water content was made on each of the clays from a sample taken after the pugging or tempering treatment. The figures given are in percentages of the weight of the dry sample and appear under "Tempering" of each test. The moisture data on this point naturally includes the water added in pugging plus the mechanical water of the original sample.

In pursuance of obtaining the water content of the clays as worked, a sample of each was placed in a glass test tube which was closed with a cork stopper and sealed supposedly air-tight with paraffine. But as over two months elapsed between the time of taking the samples and that of making the determination, the results may

be a trifle low. But they should at least be fairly comparable and adequate for all purposes here desired. The laboratory procedure was as follows: Samples averaging 2.5 g. were weighed out in porcelain crucibles and placed in a jacketed oven previously heated up to a constant temperature of 110° C. After remaining at this temperature for 1 1/2 hours they were again weighed and the loss in weight calculated in percentage of the dry weight. Further comments upon the results will be reserved for the conclusions of this paper.

The clays were given whatever grinding treatment necessary and when disintegrated the pugging imposed

was excellent, being better in fact than would be given in commercial practice. The clay was spread out in a thin layer on the floor of the testing room and water was added in small amounts at a time, mixing the mass thoroughly with a shovel. The auger machine equipped with standard knives and single auger was used in tempering the clay and the homogenizing treatment imparted by this apparatus was of a higher grade than that of an ordinary pug mill. A 3 inch by 4 inch wood piece into which two 7/8 inch wrought iron rods were set, bolted on the nozzle extension, broke up the column of clay as it was forced from the machine. This action, together with the "cutting up" given by the knives and auger, make the pugging quite efficient. Plate XIII is a photograph of the auger machine with pugging attachment.

Each batch of clay was passed through the machine a sufficient number of times to give uniformity in consistency and water content and to be in the best condition for further manipulation. It might be well to state that in all the tests the clays were worked through the dies in as stiff consistency as conditions would allow. The tendency of a stiff-tempered clay is to flow better through a die than a soft material as the former forces the preceding parts of the column through the die more uniformly and gives a more perfect cross section than the latter. Also in working a clay as stiff as possible the resultant product is more easily handled without marring and no necessity is imposed of expelling, in the drying operation, any of the unnecessarily incorporated moisture.

PHYSICAL TESTS OF CLAYS.

MATERIAL NO. 1.

Description of Sample.

A soft yellowish-tan drift clay from Mill Bank, Fort Beaufort, Eastern Province Cape Colony, South Africa. It was a nonstratified material, very fine grained and contained no pebbles or foreign particles which might be expected to complicate results.

The material being a surface clay was quite easily pugged, it taking water well and developing a good grade of plasticity. The tempered clay was of a "fatty" nature but not to such an extent as to be sticky and to cause die trouble from that source in the subsequent tests. As worked the clay contained 15.47% moisture.

Method of Procedure.

Trial 1. On Die No. 1 (Plates IV and V) lubricating with steam. The clay column produced was ragged or spurred out at the upper corners, the cracks extending about 2 inches on each side away from the corners (Plate XIV, Trial I.)

Trial 2. The second attempt was with Die No. 2 lubricating with water, which was conducted to the chamber

around the liners from a reservoir about two feet above the die. The use of a reservoir eliminated the possibility of marring the clay column by a too great water pressure and also served as a pressure gauge, the force of the water although undoubtedly slight, being constant at all times. The results with this equipment were even worse than those obtained in Trial I. The same spurring out of the corners was experienced but to a greater degree than in the first trial (Plate XIV, Trial 2). The deep vertical cracks noticed on Trials 1 and 2 were caused through drying out of the clay bar before the photograph was taken, and are not defects imparted by the dies.)

Trial 3. On Die No. 2, but using steam lubrication. Steam was used on this die purely as an experiment and not as a matter of regular procedure. The corners were again bad, but the trouble was of a different nature than heretofore experienced. Instead of spurring up, the corners did not come out full, but were roughed up corduroy-like with frequent deeper indentations, the clay refusing to take to the corners and flow full (Plate XIV, Trial 3). The cause of these two corner imperfections cannot be definitely stated, but Trial 2 showed bad corners developing in the bar when the clay left the die, the friction tending to draw them outward like the shavings from a draw knife. In Trial 3 the clay either did not take to the corners at all or some particles lodged there so persistently that the following material could do nothing but flow past these impeding portions and give a column lacking in cross section at these points. At any rate the defect took form within the die and not merely at the point of leaving it.

Trial 4. On Die No. 2 using as lubricant a mixture of 1/2 machine oil and 1/2 kerosene fed from the before described reservoir. This attempt gave results similar to Trial 3, but not bad to such a great degree (Plate XVI, Trial 4). At this juncture it appeared that the demands of the clay could not be met with a long die as the material could not withstand the corner friction of such

PLATE XVI.

without defects. The author surmised that better results would be obtained with a shorter die and its consequent less friction. In other words it was expected that a short die would reduce the friction, facilitate the corner flow and still perform its primary duty of imparting a rectangular shape to the outflowing material. Bearing these points in mind Trial 5 was made.

Trial 5. On die No. 3 (Plates VIII and IX) which was a steam lubricating, short die. A better clay column was formed than in any of the previous trials, without spurring out or hollow spots in the corners (Plate XVI, Trial 5). The whole die area well filled with clay but the column zig-zagged on account of the short die setting too close to the end of the auger. As the auger revolved, first one side and then the other side of the column pushed forward, thus cracking it transversely from unequal pressures. There was not sufficient distance where stated to allow the thrusts of the auger lip to equalize themselves within the confines of the nozzle extension and die. Hence the auger pressure, alternating, as it were, resulted in zig-zagging or a wavy column. In other words the focus of the auger screw was not correctly provided for.

The photograph of a portion of the column of this trial does not well illustrate the points brought out in the preceding discussion on acount of drying cracks developed before the photograph was taken. For instance the longitudinal crack in the center of the column did not show up when the clay left the die,but its appearance later strengthened the conclusion of unequal thrusts inadequately taken care of. This drying cracking also illustrated how imperfections caused by the auger may remain concealed until drying or even in some cases burning, brings them to light. If the clay particles are arranged under conflicting stresses, sooner or later they will assume a normal equilibrium, and in so doing cracks will occur.

Trial 6. At this point while waiting for a piece of apparatus to use in the next trial with a side cut die, a run was made on Die No. 4, an end cut dry die (Plates

X and XI). The result requires no comment as a perfect smooth column was obtained without difficulty (Plate XVI, Trial 6).

Trial 7. On Die No. 3 with steam lubrication (Plates VIII and IX). As explained before, the defects of Trial 5 were caused by the die setting too close to the auger and presumably not from any fault of the die itself. In order to prove this assumption a wooden ring 1 3/4 inches thick was bolted between the nozzle extension and the die, thus bringing the die forward that distance. With this fitting the column had a uniform flow throughout without the waving motion, but other defects heretofore absent now presented themselves (Plate XVII, Trial 7). The column split vertically in the center immediately upon leaving the die and flowed with a "V" shaped opening between into two bars. The corners also had long cracks extending arrow-head like from the intersection of the surface planes. This splitting of the column was attributed to the effect of the single thread auger while the corner cracks were different from those obtained when the clay refused to flow smoothly on account of friction as they were farther apart and the clay between them did not spur up ragged-like. They seemed to be due to transverse strains set up in the column by the unequal push of the single lip auger. Hence the necessity of using a double screw auger appeared.

Trial 8. On Die No. 3 with steam lubrication (Plates VIII and IX). The machine was equipped with a double thread auger (Plate III), but the 1 3/4 inch wooden ring was omitted as it was thought that this type of auger would take care of the defects for which the ring was used to remedy in Trial 7. It could be expected that the thrust of the two lips would materially reduce the zig-zag flow and also prevent the central longitudinal cracking of the column. As far as forward pressures are concerned an increase in the number of threads or discharging lips on an auger makes the effective thrust more nearly like that of a piston or plunger. Hence in this

case a double thread auger should show improvement over a single thread one.

Actual developments proved the above conclusion to be correct. The corners were well filled and ran true, cracking very little. But the bar cracked vertically on alternate sides about every 5 inches or 6 inches corresponding to each revolution of the auger (Plate XVII, Trial 8). The illustration does not show these cracks as the portion of the bar shown happened to be a piece broken from the column where two succeeding cracks occurred. The fact

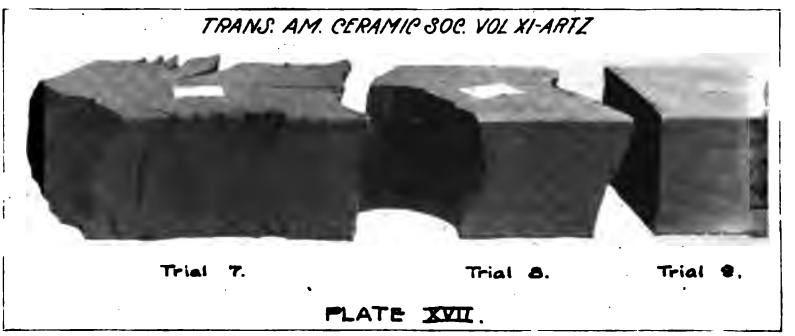


PLATE XVII.

that a good column exclusive of these vertical side cracks was obtained, centered the trouble not in the construction of the die or the lubrication, nor not necessarily in the double thread auger but rather attributed it again to the position of the die with reference to the auger.

Trial 9. On Die No. 3, steam lubrication, with double thread auger and 1 3/4 inch wooden ring between the nozzle extension and the die. This outfit gave a good even flow of clay, full square corners and in fact a perfect column (Plate XVII, Trial 9.)

Conclusions on Test.

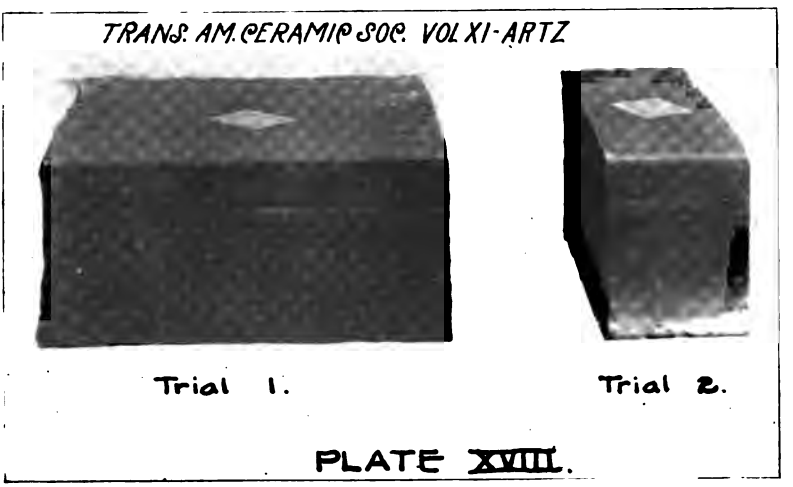
The material could be worked equally well on a side cut or end cut die. With the end cut die a single thread auger was suitable but in running a side cut column a

short die and double thread auger was necessary. But in that case the die had to be correctly located by means of the wooden ring.

MATERIAL NO. 2.

Description of Sample.

A soft steel-colored shale from Weir City, Kansas. The clay was mediumly fine grained but it contained a considerable number of hard pebbles varying in size from 1/8″ to 1/4″ in diameter.



Tempering.

The material was pugged three times through the auger machine fitted with the end illustrated in Plate VIII. A rather tough plasticity was developed and the clay was tempered to the stiffest possible workable consistency. The moisture determination gave a result of 16.61% mechanical water.

Method of Procedure.

Trial 1. The material was first tried on Die No. 1 with steam lubrication (Plates IV and V). The results showed a marked difference from those obtained in the first part of Test No. 1 on the soft drift clay. Here a sound, perfectly formed clay column was immediately procured and a run of five minutes developed no flaws in the bar (Plate XVIII, Trial 1).

Trial 2. On Die No. 5, a side-cut, steam-lubricated paving block die. As this die so closely resembled Die No. 1, no photograph of it was taken. As the material behaved so well on Die No. 1 no difficulty was expected from this larger die and this conclusion was correct as the column was of equally good quality as that in Trial 1. (Plate XVIII, Trial 2).

Conclusions on Test.

The material was very easily run, flowed well and gave a good column under simple conditions. There was every reason to believe from its behavior on side-cut dies that it would work well on an end-cut die also. On account of its adaptability to being worked quite stiff it filled the die well and made good square corners. The surface of the bar also took a high polish and the lubricating film formed by the steam made easy flow possible. As a rule clays which attain a high degree of polish from the die can be worked with equally good results by water lubrication as well as by steam and in this case such was quite probable.

MATERIAL NO. 3.

Description of Sample.

An already-ground steel-colored shale from Dallas, Texas. On account of the material being ground no opportunity was given of satisfactorily studying its original physical structure. But it contained no evident impurities such as pebbles, hard minerals, etc.

Tempering.

The material was pugged well in the auger machine (Plate XIII) developing a plasticity rather of the sticky type. But it had very little bonding strength, breaking along irregular surfaces and having a soapy, lustrous, plate-like fracture. The mechanical water in the material as worked was 22.97%.

Method of Procedure.

Trial 1. On Die No. 1 with steam lubrication (Plate IV and V). The material was quite sticky as before stated and a very poor column was obtained (Plate XIX, Trial

PLATE XIX.

1). The corners ran round and cracked while the sides, top and bottom of the bar were scaly, having been made so by the material sticking to the die. When more steam was used to give better lubrication the column became too soft and wet to travel well or to handle. The trial showed evidence throughout of the scaly nature of the clay and it laminated badly from the auger. But as the object of these investigations concerned the flow of clay only, the author made no attempt to study or to reduce this lamination.

Trial 2. On Die No. 3 with steam lubrication (Plates VIII and IX). A considerable amount of steam had to be used or the column would be impeded in the die and upon

coming out the corners would spur up very badly. As it was worked a fair column was obtained but not a perfectly smooth one (Plate XIX, Trial 2). On account of the short length die and single thread auger the bar zig-zagged or waved slightly. But as the clay was quite wet, this side motion did not break the column. Nevertheless it was objectionable for evident reasons.

Trial 3. On Die No. 3 with 1 3/4" wooden ring between the nozzle extension and the die in an attempt to eradicate the waving motion of the column. This application corrected that fault and gave a straight running bar and full true corners, but the matter of lubrication had to

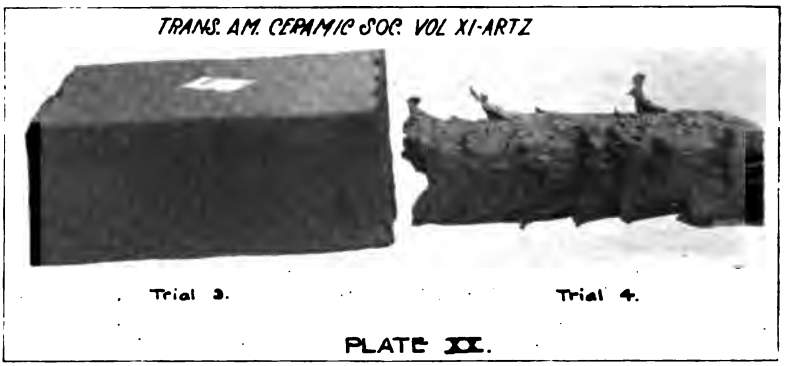


PLATE XX.

be taken care of as in Trial 2 (Plate XX, Trial 3). The column was good but not quite of the highest quality as pertained to smoothness. The lamination was the only defect in structure and the bar would have afforded suitable blocks for repressing. But it is doubtful whether the best quality wire cut brick could have been made on account of the surfaces being under grade in smoothness. Naturally it is to be understood that in speaking of commercial products that the matter of auger lamination is out of consideration.

Trial 4. On Die No. 4 an end-cut dry die (Plates X and XI). Exceedingly poor results were obtained (Plate

XX, Trial 4). The illustration shows the column traveling from right to left instead of the reverse as in the proceeding photographs. The corners were ragged and spurred up and the entire surface of the bar was greatly roughed up.

Conclusions on Test.

The test showed that the material was not valuable as a commercial proposition even though fairly acceptable results were obtained in Trial 3. On the whole the clay was too sticky and exhibited a tendency to leave the die in a marred state under almost all conditions. When this defect was modified by increased lubrication the surface of the bar became too soft and wet to be handled conveniently. The trial on the end-cut die condemned it completely for that type of manufacture and in both side-cut and end-cut the highly developed laminated structure was strictly against its commercial use.

MATERIAL NO. 4.

Description of Sample.

A yellowish-brown weathered shale from Oakland, California. The material was rather soft on account of being weathered, but it contained a few small hard pebbles.

Tempering.

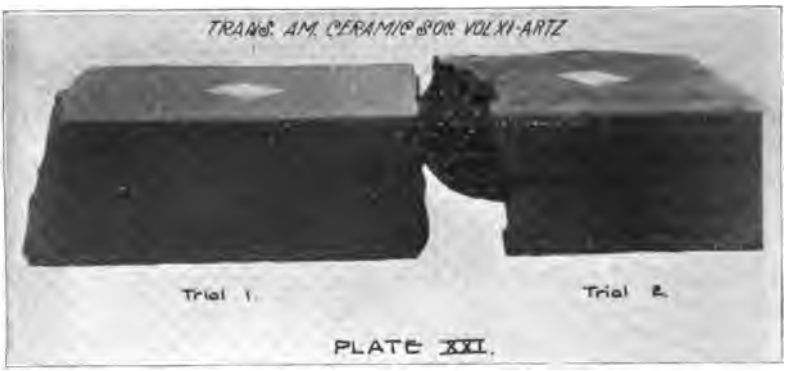
After pugging thoroughly in the usual way of the preceding tests the clay developed a medium sticky plasticity but it required a considerable amount of water in the process. The subsequent determination of mechanical water showed 22.71% moisture. To obtain the best results the material was worked in the following trials at a quite stiff consistency.

Method of Procedure.

Trial 1. On Die No. 1 with steam lubrication (Plates IV and V). The clay flowed perfectly at the first attempt,

the corners being full and true, the surfaces smooth and the internal structure without flaws (Plate XXI, Trial 1).

Trial 2. On Die No. 5, the steam lubricated paving block die (not photographed). The results were equally as good as obtained in Trial 1, for the die conditions in both cases were similar (Plate XXI, Trial 2).



Trial 3. On Die No. 2 with water lubrication. Here again the column was satisfactory and of good quality, the water lubrication acting equally as well as did the steam. As regards appearance the samples of the results of the three trials were so similar that no photograph was taken of a portion of the bar from Trial 3.

Conclusions on Test.

The clay was very easily worked, no lubrication difficulties being encountered. Nature's weathering made possible a development of plasticity and smooth column flow with but a minimum amount of mechanical tempering. Indications pointed to the attainment of just as good results with dry dies producing end-cut brick, hollow ware or drain tile, as with lubricated dies. So nothing but the best can be said of the working qualities of the material.

MATERIAL NO. 5.

Description of Sample.

A soft, red alluvial clay from Dayton, Ohio, containing a considerable amount of stones, roots and small pieces of vegetable matter. This clay is used in the manufacture of common building brick, made by the soft-mud process. Attempts have been made before to work it stiff-mud but all have failed for reasons which are presented in the following description of the trial made.

Tempering.

The clay was easily pugged, developing a minor grade of sticky plasticity when considerable water was used. But when this point was reached the material was much softer than that used in ordinary stiff-mud practice. By the use of only a small amount of water plasticity was not sufficiently developed and the material was quite tender and of low bonding strength. As experimented with, the clay contained 21.13% mechanical water.

Method of Procedure.

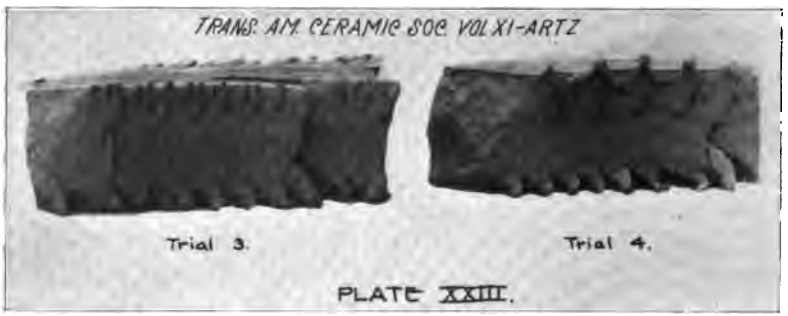
Trial 1. On Die No. 1 with steam lubrication (Plates IV and V). All four corners spurred up although the bottom, top and sides ran smoothly. This latter fact showed that those points were sufficiently lubricated but the tenderness of the material prevented the corners from being forced out intact (Plate XXII, Trial 1.) If more steam

PLATE XXII.

were used the bar became soft and soggy without the corner friction being reduced and the excess of lubricant would entirely wash away the corners of the column in the die and only the center core of the bar would be forced from the die. Seeking to reduce the quantity of friction without the necessity of excessive lubrication the next trial was made.

Trial 2. On Die No. 3 with steam lubrication (Plates VIII and IX). Here the corners spurred up in large saw tooth fashion to a much more marked degree than in Trial 1 (Plate XXII, Trial 2). Differential auger pressures, magnified by the short length die caused the column to crack diagonally from the sides.

Trial 3. On Die No. 3 with steam lubrication using the 1 3/4″ ring to bring the die farther away from the auger in pursuance of reasoning established in Test No. 1,



Trial 7. By this means the diagonal cracks were diminished in extent but the corners were still very poor on account of the die friction (Plate XXIII, Trial 3).

Trial 4. On Die No. 2 lubricating first with water and then with soap water by means of reservoir above the die. The worst results of the test were obtained here. Not only were the corners bad, but there was a vertical break or crack in the center of the bar parallel to its travel caused by the retarding influence of the clay holding in the cor-

ners and thus pulling the column apart (Plate XVIII, Trial 4). The soap water did not prove any better lubricant than the water above.

Conclusions on Test.

Briefly speaking, the clay had a too low bonding strength when tempered to a stiff enough consistency to be worked through a die in a continuous clay column. It was only upon the addition of considerable water that this leanness was overcome. But by so doing the condition of the material became so soft that the pressure of the column could not force the preceding parts from the die without being too seriously affected by the die friction. The clay was a strictly soft-mud material, for it is just the qualities above mentioned that put a clay in that class. Even had an acceptable column been obtained the dense structure caused by the stiff nature of the body would have caused cracks in drying. Although this last point is a digression from the subject, drying a block of the stiff-mud formed clay showed it to be a fact.

Hence, when a clay behaves like this one, showing no indications of working satisfactorily it would be well to class it as being suitable only for the soft-mud process of manufacture.

MATERIAL NO. 6.

Description of Sample.

A soft gray weathered shale from Cattaraugus, N. Y. The shaley structure was evident but not pronounced, having been destroyed to a great extent by the weathering. The material was free from stones, hard minerals, etc.

Tempering.

A good grade of plasticity of a character common to soft weathered or argillaceous shales was easily developed and as worked the material contained 25.96% moisture.

Method of Procedure.

Trial 1. On Die No. 1 with steam lubrication (Plates IV and V). Such perfect results were obtained at this first attempt that no sample was saved or photographed.

Conclusions on Test.

A very reasonable conclusion to make is that this material lends itself quite well to the stiff-mud process with steam lubrication and it would undoubtedly have behaved equally well with water lubrication or in the forming of hollow wares by means of dry dies.

CONCLUSIONS.

In the flow of plastic clay through dies the three factors as originally stated, which may be varied at the will of the operator are the mechanical equipment (the die, auger and knives), the lubricant, and the preparation (tempering) of the material. The inherent quality of the clay is a constant factor, its behavior being governed by imposed conditions of manipulation. It is true that grog is sometimes used to reduce the plasticity of a clay and to facilitate its working. Hence, the seemingly broad statement that the external conditions only are susceptible to change.

Since each clay presents individual characteristics it is extremely difficult to generalize upon them. As in any case where one is working more or less in the dark, it is well to select some arbitrary conditions for the first trial in a clay test and then from the results obtained, endeavor to locate the seat of the faults and remedy them by successive changes in the imposed conditions. By careful observation and some practice the cause of imperfect clay flow can generally be attributed to a certain unsuitability of the apparatus used and, in the nature of the case, one can conclude what alterations in such would improve results.

It is the opinion of the author, borne out by facts, that the kind of lubricating substance is of much less consequence than the form or lines of the die reducing the friction. Poor results might also arise from improper tempering or consistency of the material but this condition can be mitigated by varying that portion of the procedure.

After having available the data on the behavior of a few clays of different types, the experimenter may often be able to take short cuts, as it were, arriving at satisfactory results without taking the intermediate steps which would otherwise be necessary.

The determination of the mechanical water in the clays as worked is of no practical value for such data carries with it no intelligible idea of how much water to add in tempering some other clay. Neither is it possible to fix the limits of the water content of a certain type of clays, i. e., to say that alluvial clays as worked possess one range of water content, shales another, and so on. In practice the water is added in more or less constant quantities in preparing a certain clay, but what the operator really cares for is the effect of this water upon the development of plasticity and the consistency of the resultant material.

The field of clays covered in this work was necessarily small both as to the number of clays tested and as to the diversity of equipment used. Throughout the report the author has endeavored to make clear the nature of the results obtained in each trial and to state the justification for concluding that certain changes in equipment or physical condition of the clays would result in improvement in the succeeding trials. Hence it is the facts submitted rather than generalized conclusions that these tests bring out.

DISCUSSION.

Mr. Stull: It seems to me rather unfortunate that Mr. Artz did not include a No. 2 plastic fire clay in his

list, because the action of this type of clay seems to be quite different from the surface clays and shales, due largely to their differences in physical make-up.

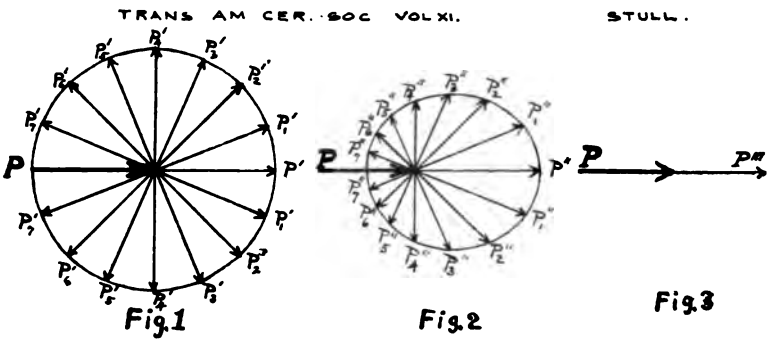
From the descriptions and illustrations of the different dies and lubricants used and the columns of clay resulting from them, it might naturally lead us to conclude that water is the worst lubricant we could employ. My practical experience in die construction, under actual practice tests, leads me to believe, without doubt, that water is the best lubricant we can employ, yet perhaps 90% of the brick makers have condemned water as a lubricant simply because it has not been given a fair trial.

The great trouble with many so-called water lubricators is that they do not lubricate. When the water lubricating die is running dry, we have about the worst form of dry die possible, owing to excessive friction due to its construction.

Clay will flow through almost any form of aperture in a more or less smooth column if tempered soft enough, whether lubrication be applied or not. Dies in operation have been brought to my notice in which the water entered the scale box under very little or no pressure, circulated freely around the scales and ran out of a drain pipe at the bottom. The clay under pressure passing through the die seals over the water openings thus giving a dry die. The column cracks if the clay is tempered as stiff as it should be in order to make the best and most uniform brick possible for the clay. Consequently, the clay is tempered softer and softer until it finally reaches the condition where the column flows smoothly, giving the erroneous impression that the die is lubricating.

According to a well known physical law a pressure applied at a given point in a perfect liquid is transmitted equally in all directions. Plastic clay may be considered as a liquid in its physical behavior, though a very imperfect one. A pressure applied at a given point in such a mass is transmitted in all directions but unequally. In

the case of the perfect liquid (Fig. 1) the transmitted forces P′, P′$_1$, P′$_2$, P′$_3$, etc., are equal to the applied force P in magnitude while in the case of plastic clay (Fig. 2) the transmitted forces P″$_1$, P″$_2$, P″$_3$, etc., in all directions except the direction of the applied force, are less than



the applied force P. If the tempering water is gradually decreased, these transmitted forces (except P″) become less and less and finally reach zero, when the clay loses the property of a fluid and takes on that of a solid, at which stage the resultant force P‴ is in line with the applied force (Fig. 3).

All those forces within the die in a direction other than that of the applied force are instrumental in sealing over or clogging the lubrication. These component forces (P$_1$″, P$_2$″, P$_3$″, etc.), may be combined into a single resultant F, perpendicular to the line of die taper, which acts in opposition to the lubricating pressure, which we will call F′. When F′ is less than F no lubrication takes place. When F′ equals F very little or no lubrication takes place. If F′ equals F+ΔF lubricating action begins. If ΔF becomes appreciably large, lubrication becomes excessive and water marking is the result.

The water pressure, F′, necessary to lubricate efficiently, depends upon the magnitude of the opposing pres-

sure, F, of the clay. F depends upon two factors, viz., the pressure P necessary to force the clay through the die and the degree of temper or viscosity. Assuming the viscosity of a perfect liquid as 0 and that of a solid as ∞ the pressure of the clay F resisting lubrication tends to decrease from the magnitude P to 0 in a direct ratio as the viscosity increases from 0 to ∞. If the column of clay is kept at a constant velocity of flow, P must increase geometrically as the temper of the clay is stiffened. Therefore, the pressure F opposing lubrication is increased in magnitude more rapidly by P than it is decreased in magnitude by increase in viscosity of the clay. This bears out actual practice, viz., that the stiffer the clay is tempered the more power is required to force the clay through the die, the slower is the speed of the column and the greater is the pressure opposing lubrication. To use a practical term, "lubrication becomes clogged."

While in the employ of a certain company making brick, we rigged up a die so that the water entered the scale box under pressure and circulated freely around the scales. The only outlet which the water had was to pass out between the scales and the column of clay (which it will do if it has sufficient pressure). This die had nearly a half inch taper. A pressure gauge placed in the line showed that a pressure of 60 lbs. of water was required to lubricate the die. By gradually reducing the taper a die was finally obtained whose taper lines were very nearly parallel. The water was under 80 lbs. pressure. By throttling down the pressure to the right degree by a globe valve it was found that the amount of water passing into the scale box was insufficient for lubrication and the column would crack. When the valve was opened wide enough in order to admit sufficient water for lubrication, the pressure became too great and the water squirted out intermittently producing water marks.

Next a pressure regulator was placed in the line which would give any pressure desired from 80 lbs. down to almost zero, at the same time supplying an abundance

of water for lubrication. For this die the pressure gauge registered 25 lbs. for perfect lubrication.

That which accomplishes the most efficient lubrication is not the water alone but a thin film of soft plastic slip formed by the water on the surface of the clay. The type of die adopted was the kind known as the "offset scale" type. The scales were made of hard cast iron finished smooth on the inside surface which came in contact with the clay. As an experiment, a set of new scales were left rough on the contact surfaces, having a coating of coarse granular sand. The natural supposition might be that these scales would materially increase the friction thus decreasing the speed of the column. To my great surprise, the result was quite the opposite. The rough surface of the scales scratched up the surface of the clay thus exposing greater surface to the water and "blunged" the clay and water into a softer and thicker film of slip, the result being a very noticeable increase in the speed of the column, and much better results in general. When the column looks shiny or glassy, you can rest assured that the water is not lubricating. When the water is lubricating properly the "glassy polish" disappears. In the case of the rough scales, the surface of the column had a dull smooth appearance as though it had been finished by rubbing it gently with a soft moist sponge.

By proper die construction and proper lubrication the column would run all day long without cracking or

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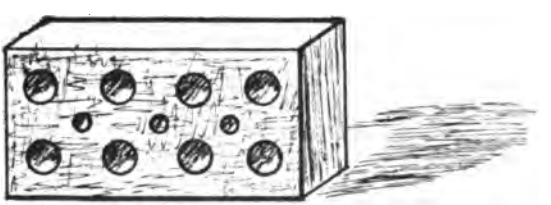


Fig. 4.

water marking. Although the clay was tempered very stiff and the brick cored out with eleven holes (Fig. 4), we were able to get an actual capacity of 17,500 brick out of a small auger machine with a rated capacity of only 12,000.

Mr. Artz's work seems to show that the best results are had with steam lubrication. With our No. 2 fire clay we could get no satisfactory results at all with steam.

THE MEASUREMENTS OF HIGH TEMPERATURES.

BY

J. K. CLEMENT, Pittsburg, Pa.

The determination of temperatures is a problem of the utmost importance in the sciences, both theoretical and applied. Thermometry is one of the oldest branches of experimental physics. As early as 1592, Galileo occupied himself with the construction of an instrument for measuring temperatures readily.

In view of the long period of development of three centuries of thermometry, it seems at first strange that many newer lines of physical measurement have until quite recently surpassed thermometry in the degree of accuracy attainable.

The reason for this is to be found in part in the difficulty of establishing a standard scale of temperature. Temperature differs from most other physical quantities in the fact that it is not additive. It is impossible by combining two bodies of known temperatures to obtain a system at a higher temperature. Whereas, two electric batteries of two volts each may be connected so as to yield an E. M. F. of exactly four volts, but if we mix two liters of water, each at 20°, the resultant mixture will have a temperature of 20° and not 40°.

The scale which has been adopted as the standard of temperature is known as the centigrade scale. Arbitrarily the temperature of melting ice is taken as zero, and the interval between this temperature and the temperature of ebullition of water under normal barometric pressure is divided into one hundred degrees. To interpolate accurately between these limits as well as to extrapolate below 0° and above 100° C., it is essential to have a substance, some physical property of which varies uniformly with the temperature. The expansion of mercury was

early recognized as being proportional to the temperature, and it is the most generally used thermometric substance.

It is known, however, that the expansion of mercury is not a lineal function of temperature, i. e., the increment of the length of a given column of mercury per degree centigrade is not the same for all temperatures.

THE GAS THERMOMETER.

The substance which most closely fulfills the requirements of a standard thermometer is a permanent gas, nitrogen, hydrogen, or helium. A thermometer using any one of these gases as the expanding medium is known as a gas thermometer. The international temperature scale is based on the constant-volume hydrogen thermometer. Since at high temperatures, 1000° C. and over, hydrogen and helium diffuse readily through walls of bulbs (platinum or quartz glass) nitrogen is generally used in high temperature thermometers.

There are in Europe and America several, perhaps less than a half dozen, standard gas thermometers, notably at Sevres near Paris, Berlin, Kew, and at the Geophysical Laboratory in Washington, D. C.

The gas thermometer, by reason of its great size and weight, the cost of installation, and difficulties of operation, is not suited for ordinary temperature measurements. It is, however, the standard to which all other thermometers and pyrometers are finally referred, by comparison, either directly or with other standard thermometers which have been compared with the gas thermometer, or by the use of certain fixed points of reference, the melting and boiling points of pure chemical substances. The accuracy of any pyrometer is then a measure of the agreement between its indications and the reading of a gas thermometer.

THE THERMO-COUPLE.

The accurate measurement of high temperature is a question of great importance in many branches of applied

science. For this purpose the variation with temperature of divers physical properties of matter has been proposed: length, heat content, electric resistance, pressure, volume and viscosity, and thermo-electricity.

In 1821, Seebeck discovered that if in a closed circuit of two metals, e. g., copper and iron, the two junctions of the metals are at different temperatures, an electric current will be generated.

In 1830, Antoine Becquerel suggested the use of Seebeck's discovery for the measurement of high temperatures. Becquerel made a couple of platinum and palladium. Pouillet (1836) made an iron-platinum couple; and Regnault (1847) investigated the same couple. On account of the unfavorable results due to the use of a low resistance galvanometer, Regnault condemned the thermo-couple and it was not until fifteen years later (1863) that Edward Becquerel revised the thermo-electric method, using a platinum and palladium couple and a high resistance galvanometer.

In 1871 Tait introduced the Pt-Ir couple, and in 1886 Le Chatelier the Pt-Rh couple. Simultaneous with Le Chatelier, Barus (1886-1889) conducted a comprehensive investigation of the thermo-electric properties of a vast number of metals. The investigations of Le Chatelier and Barus, and later (1899) of Holburn and Day, established the thermo-couple as an accurate instrument for temperature measurement.

The platinum-rhodium couple is the most reliable couple for high temperatures. Its range is from 300° to 1600° C. For lower temperatures, 0° to 500° C., the copper constantan couple is available.

In the last few years a number of couples of base metal alloys have been placed on the market. Their range is limited, the upper limit varying from 1000° to 1400° C. So far as I know, little information has been published regarding the accuracy and reliability of these couples.

MEASUREMENT OF E. M. F.

Two methods are in use for the measurement of the E. M. F. of thermo-couples:

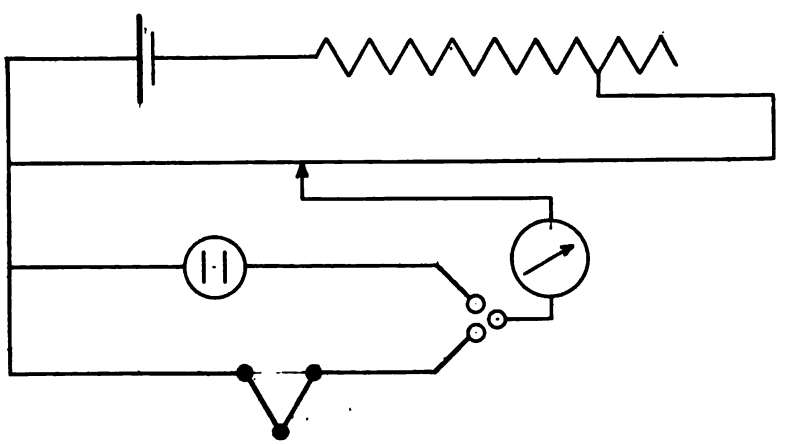
1. The Galvanometer method.
2. The Compensation or Potentiometer method.

The former is by far the simpler method and it can be used by any intelligent operator and requires no special knowledge of the laws of electricity. Its sensibility is considerably less than that of the potentiometer method: 1 scale division=10° C.

With a high resistance galvanometer, 400 ohms, and proper precautions, the observations are reliable to about 5° up to 1100° C., and above this temperature to 10° or 15°.

Many of the millivoltmeters now on the market for use with thermo-couples,—all pivoted instruments,—are of low resistance, less than 5 ohms. With such instruments the reading is dependant very largely on the resistance of the couples and leads, and since this varies with temperature and length of leads, the low resistance instrument cannot be recommended for precision measurements.

The galvanometer method can be adapted to recording the temperature, by having the needle attached to the moving coil carry a pen point.



Application—kilns, glass pots, etc.

Potentiometer Method. The principle is illustrated by the following diagram:

For accurate laboratory measurements the potentiometer method is to be recommended. The sensibility is 1 M V=0.1° C.

The installation required consists of:

1. Potentiometer.
2. Standard cell.
3. Galvanometer.
4. Storage cell.

A third method of measuring the E. M. F. of a thermo-couple, which is capable of higher accuracy than the galvanometer method and is less cumbersome than the potentiometer method, is the current compensation method. Lindeck has designed an apparatus involving this principle.

The formula for the E. M. F. of the Pt.-Rh. couple most generally used is $E = a + bt + ct^2$.

CALIBRATION.

In general no two thermo-couples have the same E. M. F., altho Heraeus has made up several kilometers of very pure platinum and platinum-rhodium wire intercouples whose E. M. F.'s agree very closely. On this account, as well as on account of the very appreciable change in E. M. F. which couples undergo when subjected to the action of metallic vapors at high temperatures, it is essential that couples be calibrated from time to time. This can be done in several different ways.

1. By comparison with a standard couple. For this comparison, the greatest precaution should be observed to insure that both hot junctions are at the same temperature, e. g., by having the couples imbedded in a large mass of metal.

2. By the determination of the points of fusion and ebullition of pure chemical substances, in particular metals. The points to be recommended are:

Cadmium	322
Zinc	419
Silver	961
Copper	1084

The values given are those of Holborn and Day, and are the ones accepted at present by the Reichsanstalt. Recently Dr. Day and myself have found somewhat lower values.

Above 1100°, nickel (1435), iron (1505), and platinum (1720) may eventually be available. Until the gas thermometer scale above 1100° has been established, it is hardly advisable to use any point above the copper point.

It is of the greatest importance that the metals used for fixed points be of the highest purity, since the melting points are altered by the presence of impurity.

For the calibration of thermo-couples by means of fixed points, two methods are in use:

1. The wire method.
2. The crucible method.

The former requires only a small amount of metal—less than a gram. The metal can be fused between the hot end of the two wires, and the E. M. F. of the couple noted at intervals as the hot junction is gradually heated. The reading immediately before the circuit is broken gives the E. M. F. of the melting point. Also, the metal, in the form of fine wire, can be wrapped about the junction of the couple and the couple introduced into a furnace heated above the melting point. At the moment of fusion the galvanometer deflection halts momentarily.

There are several objections to this method. The metal fusing in contact with platinum wires is certain to alloy with the latter, thereby making them more readily fusible, besides altering the E. M. F. of the couple. Also,

if the fusing metal is heated in the air, it is liable to oxidation, and a consequent lowering of the melting point.

The crucible method is free from most of these sources of error. Holborn and Day used crucibles of porcelain and graphite of about 300 or 400 grams capacity. In most cases, iron excepted, graphite is preferable. In cases where the metal used is susceptible to oxidation, e. g., silver and copper, it is necessary to further protect against oxidation by a layer of powdered charcoal or graphite, or by heating in a reducing, (CO), atmosphere.

Frankenheim Method: The couple, enclosed in a porcelain or quartz glass tube, is emersed in the metal, the furnace allowed to cool slowly, and the E. M. F. observed at regular intervals (30 seconds or 60 seconds). During the process of solidification the E. M. F. will remain constant; similarly during fusion.

Sources of Error: The error most frequently overlooked and easiest to correct is that due to the variation in the temperature of the cold junction. For laboratory measurements, the cold junction should be maintained at zero degrees. In commercial work it should be maintained at a constant temperature if practicable, e. g., 100° centigrade. Otherwise, the temperature of the cold junction should be noted and the correction applied: $t = tobs + 0.5\times$ temp. cold junction.

An error, almost inevitable under practicable working conditions, is that arising from the contamination of the wires and their consequent inhomogeneity. Metallic vapors, iridium especially, readily attack platinum, producing a change in its thermo-electric properties. The drop in the E. M. F. due to contamination may amount to 50 degrees, or even 100 degrees centigrade. It is therefore highly desirable that when couples are used in furnaces in which slagging materials or reducing gases, or both, are present, the wires should be enclosed in a protecting tube, wrought iron, for example.

A couple once contaminated cannot be restored to former conditions except by removing the injured portion. The readings of a couple, when it is new and free from impurity, i. e., homogeneous, are independent of the depth of immersion. In a contaminated couple it is necessary to avoid temperature variations along the wires, since the inhomogeneity produces a condition in which the couple behaves like a series of almost infinitesimal couples. In the calibration of a contaminated couple, the depth of immersion should be the same as in working conditions.

A fourth source of error, brittleness in the wires, can be remedied by annealing.

All these sources of error make it necessary that couples be calibrated at frequent intervals.

It may be well to call attention to two further sources of error in temperature measurements, which, however, are not in the thermo-electric circuit. In furnaces operating under reduced pressure, the entrance of cold air through an opening around the pyrometer tube will produce a lowering of temperature. Also in the measurement of the temperature of gases, a low temperature may be produced by the conduction of heat along a tube or wires, and by radiation to cooler walls.

The sensibility of platinum-rhodium couples is 0.1° with the potentiometer and 5° to 10° with the galvanometer.

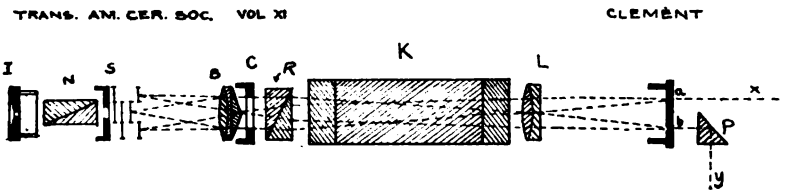
The accuracy with the potentiometer is about 1.0° below 1100°; with the millivoltmeter about 5°, when all precautions are observed. An accuracy of about 25 degrees can be obtained with ordinary conditions providing the couple is in good condition.

WANNER OPTICAL PYROMETER.

Above 1600° C., and in many cases above 1200° C., the optical pyrometer has to be used.

The Wanner pyrometer is used very extensively. The

principle of this instrument is shown in the drawing. The Wanner pyrometer is easy to operate and when properly standardized by means of the amylacetate lamp, which is furnished with it, is capable of relative accuracy of 5° to 10° C.



a, b—Slits.
x—Light from comparison source.
y—Light from incandescent lamp.
P—45° prism.
L—Lens.
K—Direct vision spectroscope.
R—Rochon prism.
C—Screen.
B—Biprism and lens.
S—Slit.
N—Nichol prism.
I—Eye-piece.

DISCUSSION.

Mr. Burt: Mr. President, there is a very practical point there which Dr. Clement has given us for remedying this brittleness. Those of us who are using instruments would be glad to know clearly the method employed.

Dr. Clement: It is done simply by heating to a white heat for a short time; but there is a detail of procedure which I may mention, namely, I wrap the two ends of the wires about heavy platinum terminals.

Mr. Burt: How long should it remain at this heat?

Dr. Clement: A short time, about half a minute. It takes some courage to carry it to the proper temperature the first time. If the couple is new it will easily stand fifteen amperes.

Mr. Binns: It does not matter which way the current goes?

Dr. Clement: No.

Mr. Frink: A little experience of mine might be interesting on the subject of optical pyrometers whereby I determined that the use of the optical pyrometer introduced errors that were not generally anticipated by people using them, viz., that in observing the temperatures of glass furnaces or any surface which reflects light or the heat rays, it takes but a slight movement of the focal or point of vision to vary the temperature some two or three hundred degrees. In fact, I have found that I have been able to focus on one point and by moving a half inch have obtained an increased reading of over 300°, owing to the fact of having changed the focal point onto a place where there was a reflection of the flame from the surface of the glass.

Dr. Clement: There are several principles involved in this question, fundamental principles applying to thermal radiation pyrometers. Where you have to do with a flame, these laws fall down, when you come to tackle that problem. To the present time, that problem has not been completely solved. Prof. Lummer of Breslau has now taken up the question of the relation of lumination to the gas laws and there may be something more reliable developed.

As to the temperature of a glass furnace, of course with the optical pyrometer you get the temperature of what you look at. If you look at the surface of the glass you get the black body temperature which will always be lower than the true temperature if we eliminate the flame factor. If the surface is actually 1800° and you measure

with an optical pyrometer the temperature reading may be several hundred degrees lower. That is because the absorption or emission constant is low, and what you get is called technically the "black body temperature," that is the temperature which a black body would have to have to radiate the same amount of energy.

Mr. Frink: You do not get the temperature of what you look at. You are looking at glass but get flame temperature minus absorption. In ladling glass, we usually endeavor to ladle at a temperature of 2050° F. It was found by actual experience that the temperature at the surface of the glass would immediately fall (or in a few seconds) from 2050° to a temperature of 1544° F. when exposed to free radiation. This is for ordinary window glass. Now, on observing the temperature by means of the Fery pyrometer or a Wanner optical pyrometer, a great variation was found from the actual readings as taken by the thermo-electric instrument. With the optical pyrometer a reading was obtained of about 1800° F., while with the thermo-electric bulb placed two inches in the glass a reading of 2000° was recorded; and from the one in the immediate surface of the glass a temperature was indicated of 1544°, as before stated. The reason for not obtaining the correct reading with the Wanner or Fery method was because of the absorption of light and heat from that mass of glass which was at or around a temperature of 2000° F. by reason of those rays being compelled to pass through a stratum of cold glass on the surface. Another instance where the optical or radiation method is valueless is that when focusing on an opening to the air, in the opposite side of a furnace, no reading can be taken; indicating that the gases through which the observation is made and the opening were at a temperature of less than 1000° F., but it is known that the furnace might or can be 2900° F. and in this instance was about this temperature.

Dr. Clement: In that case, with the melted glass more or less transparent, I should say it would be out of the question to measure the temperature with an optical pyrometer, though it might give you some guide.

SOME NOTES ON THE MECHANICAL ANALYSIS OF CLAYS.

BY

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The important influences which the size of the particle of clays or materials used with clays has upon their various physical properties such as shrinkage, fusibility, porosity, rate and safety in drying, safety in burning, color, plasticity, etc., have been recognized and reiterated by all investigators. So universal has been the recognition that references to literature would probably include all investigations having to do with the physical properties of clay. Notwithstanding the common agreement as to the importance of this condition, still there has been comparatively little done in the study of the subject and that has been, for the most part, by a variety of methods of varying accuracy.

This fact was brought clearly to our attention in the laboratory of the Department of Ceramics at Rutgers College during the past year by the extraordinarily widely varying results obtained by the use of an apparatus recommended for sizing material. Since then we have given considerable time to a comparison of the various methods generally recommended. Only a brief description of these methods will be given, since more detailed descriptions may be found in several places—notably, *Agricultural Analyses, Vol. I,* by Wiley.

Clay ordinarily comes to the user in the form of lumps of easily friable material which may be brought into complete suspension in water after thoroughly softening it by slaking and then stirring or shaking the mass vigorously.

Flint, spar and stone, which are the other materials, in ordinary use, are to be had in a finely ground condition. These particles whether of clay or ground stuff differ among themselves physically in the following particulars:

1. Size.
2. Specific gravity.
3. Form.

With respect to size and form they differ widely. In specific gravity the common minerals found in clays differ only slightly, as appears in the following table—"Clays, Occurrence, Properties and Uses"—P. 136, Ries:

Kaolinite	2.6
Calcite	2.7
Biotite	2.7—3.1
Quartz	2.65
Feldspars	2.55—2.75
Mica (Muscovite)	2.76—3.

It is therefore impossible to separate these minerals by any known method depending upon differences in specific gravity. The methods which are in use therefore depend upon differentiating between particles of different size and form and not upon mineral composition. These methods may be classified as follows:

1. Subsidence, or beaker method—often referred to as the Osborne or Whitney methods.

2. Elutriation—Schultze method, Schoene method, Hilgard method.

3. Centrifugal method—Yoder method, as used by the U. S. Dept. of Agriculture.

4. Pneumatic method.

5. Miscroscope method—Sizing by counting.

6. Miscroscope method—Using stains.

THE SUBSIDENCE METHOD takes advantage of the differing rates of fall of bodies suspended in water at rest. The mode of operating is to bring the whole material into suspension in water and after permitting it to stand a few

minutes the fluid, still containing particles in suspension, is decanted from the larger particles which have settled. This is repeated with varying periods of subsidence. The coarse particles settle after short periods, depending upon their size, and fine particles require increasingly long periods.

THE ELUTRIATION METHOD involves the use of a moving column of water, which will transport bodies of various size depending upon the velocity of the current. A variety of apparatus has been devised for this purpose by agricultural chemists, the most important of which are the following:

The Schultze Apparatus.—The original apparatus consisted of (ordinarily) three funnel-shaped glass or metal receptacles. The apparatus used by us was cylindrical with funnel-shaped bottoms. (Trans. A. Cer. Soc. Vol. VIII, 247). These cylinders were of equal height, but varying diameter. A constant flow of water is maintained through the apparatus from the smallest, through the intermediate into the largest receptacle. With this arrangement the velocity is greatest in the first or smallest can, and diminishes to the least in the last or largest can. The theory is that the diameter of these cans and consequently the speed of flow is proportioned to the hydraulic value, i. e., the particles that cannot be transported by the diminishing flow remain behind. The coarsest particles will be found in the smallest can, the next range of size in the intermediate, and the finest in the largest can. Of course, there will remain in suspension in the largest can a very fine portion which is lost through the overflow.

The Schoene Apparatus differs from the Schultze in form,—the principle is the same. The velocity of the flowing water for each hydraulic value is controlled by a gauge. Our experience has been that capillarity in the piezometer

vitiates to a large degree the delicacy of this control for the small particles. We found it necessary to disregard the piezometer and to measure the outflow. The apparatus has been too frequently described to require further detail.

The Hilgard Apparatus differs from the Schoene in two important particulars; namely, the cylindrical tube for the elutriation, and the use of a set of arms in the tube, which are mechanically rotated at a high speed with the purpose of breaking up all flocculations.

THE CENTRIFUGAL METHOD (U. S. Dept. Agric. Bureau of Soils, Bul. No. 24) is, as indicated by the name, the separation of various sized particles in suspension in water by the use of centrifugal force. A modification of this, devised by Yoder, (Bulletin 89. Utah Expt. Station, 1904) combines at the same time, elutriation with the centrifugal separation. Only the finer portions are separated by the centrifuge. The remaining particles are separated by subsidence.

PNEUMATIC SEPARATION.—Proposed by Cushman. The particles are sized dry by currents of air of differing velocity.

MICROSCOPE.—During magnification of a portion of the sample, the particles may be measured and counted and an estimation made of the proportion of the various sizes.

The use of stains has been proposed.

The agricultural chemist has been the deviser of methods for such tests and the ceramic chemist has adopted them. In looking over ceramic literature regarding this matter, one usually finds the Schoene method given precedence. The subsidence method ordinarily is only briefly discussed. The Hilgard apparatus is sometimes described and only in the newer works is the centrifugal method advocated. In all state reports on clays, the importance of size upon properties is specifically

recognized, but not much attention has been given to methods. I have found the following methods used:

Iowa report—The Whitney or subsidence method.
Maryland report—The centrifugal method.
Wisconsin report—The use of the microscope.
South Carolina report—No method described.
Connecticut report—No method described.
North Carolina report—No method described.
Alabama report—No method described.
West Virginia report—The centrifugal method.
New Jersey report—The centrifugal method.
Michigan report—No method mentioned.
New York report—Elutriation principle described; no method specifically mentioned.

Missouri report—Rate of slaking advocated as an indicator of degree of fineness.

It should be said in fairness that some of the above mentioned are merely reconnoisance reports. But it is to be noted that all give far more attention to chemical analyses, which are of little value as compared with the mechanical. "The lack of regard for the physical properties has been one of the chief reasons why science has not been able to explain many peculiarities of clay bodies, and that the conclusions derived from a chemical analysis were often in direct contradiction to practical experience; and if these gaps cannot be at once filled out, the cause for it lies in the fact that comparatively few, and for the most part incomplete, investigations are at hand." These are the words of Seger.

Regarding opinions as to the various methods, we find these statements:

The Subsidence or beaker method:

Hilgard (Report of the work of the Agricultural Experiment Stations of the University of California, 1891--1892 pg. 248) says that this requires too close attention, therefore is not suitable when a large number of analyses are to be made.

Ries (Report on the Clays of New Jersey, 1904 p. 107) says that settling is the simplest and least accurate.

Osborne (Wiley, Agricultural Analyses, Vol. I, p. 240, quotes from Connecticut Agricultural Experiment Station, Annual Report 1887, pgs. 145 et seq.) finds that the beaker method gives results practically identical with the Hilgard apparatus on sands and silts of pure quartz or similar resistant material. With coarse sands and silts upon whose grains finer matter has been cemented by silicates, etc., and with soils containing slaty detritus, the churn elutriator with preliminary boiling may give results too low for coarse and too high for finer grades. In these cases, beaker elutriation with pestling yields more correct figures. With the beaker method flocculation of particles occasions little inconvenience and does not impair the accuracy of the work.

The difficulty inherent with this method is due to the following cause. When a fluid containing clay in suspension is allowed to come to rest and subsidence begins, the small particles near the bottom have not so far to fall as those of the same size near the surface, consequently some small particles must be carried down with the large. Therefore one subsidence for any given size will not be sufficient, but the residue after decanting must be repeatedly brought into suspension and allowed to subside until the fine are separated from the coarser particles.

The Schultze method has been found inaccurate because of the eddies caused by the flowing water transporting particles beyond their proper place of subsidence, and the tendency towards flocculation. Hilgard (op. cit.) found the Schoene apparatus much more satisfactory than Nobels, which is similar to Schultze, provided that the colloidal clay was first removed, but even then there remained a large and variable residual error.

The Schoene and Hilgard methods of elutriation proved so greatly superior to the Schultze method as to entirely supersede it.

Mitscherlich (Bodenkunde, p. 47) says that only if the particles have a spherical form and the same specific gravity can one quantitatively separate by elutriation the coarse and fine particles. He concludes that since this condition does not exist, therefore, the elutriation method is unreliable.

Osborne (Wiley p. 246) says that the Schoene apparatus will give fairly correct separations with sandy soils containing little clay or matters finer than 0.01 mm, but on loams rich in humus or clay it gives grossly inaccurate results. It is not superior to the beaker method either in economy of time, accuracy, or ease of operation.

Mitscherlich (Bodenkunde, p. 46) speaks of the Hilgard apparatus as one of the best known, probably on purely theoretical basis.

Wiley (Op. Cit. p. 247) in general conclusions regarding the various methods says that the Hilgard and the Osborne subsidence methods are to be preferred to all others. The Osborne method is to be preferred to the Hilgard for simplicity and speed. When carefully carried out the results of the Hilgard and Osborne methods are fairly comparable. For rigid control the Hilgard method is to be preferred.

Seger (Vol. I p. 44) noted the liability to error of the Schoene apparatus for the separation of the finest washed substance from the sandy and silty part, but less liability to error in the separation of the coarser grained materials which require the application of a greater velocity.

Inherent faults of the elutriation method are: 1. The large volume of water required which ordinarily must be more or less impure, and probably introduces soluble salts or organic matter. 2. The long time required for the analysis. 3. The troublesome manipulation to break up flocculations. 4. The rather fragile apparatus.

The centrifugal method, as used by the U. S. Department of Agriculture, is undoubtedly the quickest, least troublesome to operate and requires less water than the elutriating methods.

The sizing by counting and measuring with a microscope as a method of analysis requires too much time, since several samples from one clay should be examined.

The use of microscope and stains has not been fully developed.

We had need during the past summer to make mechanical analyses of several clays and casting about for a simple automatic process we tested first the Schultze method.

The apparatus used consisted of three copper cans, as described in Vol. VIII, p. 247 of the *Transactions*.

The water used was drawn from a tap, run through a large filter made up of layers of small pieces of coke, absorbent cotton, bitstone and glass sand, and supplied to the apparatus by a constant level device.

The apparatus was calibrated by putting into it a sample of ground flint and after elutriation, examining the various residues under the miscroscope to determine their size. After a few trials it was found that a delivery at the overflow at the rate of 160cc. per minute did not carry off particles greater in size than 0.01 mm.

To test a sample of clay, we used 20 grams which were thoroughly shaken in a flask with about 90 cc. of water until all was in suspension. This portion was washed through a 200 mesh sieve and the portion passing through was washed into the Schultze apparatus at the same time that a current of water was flowing into the same reservoir. The results which are given below show some very wide variations and some close agreements.

Mechanical analyses of Stoneware Clays. Schultze App.:

		Clay	Rock Dust	Fine Silt	200 Mesh Sand	Residue
M1	Furman, original	94.32	2.63	0.23	0.59	2.23
M2	Furman, original	93.62	2.94	1.09	0.31	2.04
M3	Furman, June Sample	78.77	15.12	1.19	1.26	3.66
M4	Perrine, original	56.23	13.80	1.10	11.40	16.47
M5	Perrine, original	55.46	15.88	1.08	6.01	21 57
M6	Perrine, June Sample	60.41	18.55	0.48	20.56	.....
M7	Perrine, Sandy	45.26	4.12	0.96	0.72	48.94
M8	Perrine, Sandy	41.15	6.51	0.73	1.71	49.90
M9	Edgar No. 9	95.00	3.37	1.06	0.35	0.23
M10	Edgar	95.97	2.74	0.39	0.34	0.56
M11	W. H. Cutter, No. 1	68.33	11.35	1.04	5.05	14.33
M12	W. H. Cutter	73.84	8.48	1.04	4.00	12.65
M13	Woodbridge Dark	86.66	11.32	1.10	0.32	0.60
M14	Woodbridge Dark	96.00	1.54	0.55	0.24	0.67
M15	M. D. Valentine, No. 1	86.41	5.30	1.53	4.69	2.07
M17	Furman, June Sample	79.64	16.63	1.57	0.93	1.23
M18	Furman, June Sample	76.19	16.29	1.07	5.10	1.36
M19	Furman, June Sample	83.05	8.99	1.19	4.55	2.22
M20	Cutter, Sandy	73.85	1.99	0.97	9.37	13.82
M21	Perrine, June Sample	68.05	6.50	1.30	12.14	12.01
M22	Cutter, No. 2 Sagger	88.66	2.91	1.61	3.33	3.50
M23	Cutter, No. 2 Sagger	83.23	9.11	1.11	3.00	3.55
M24	Cutter, Sandy	71.50	3.54	0.60	8.70	15.66

Owing to the too frequently recurring inaccuracies which we thought possibly due to the flocculation, we tried the experiment of first separating the clay with a centrifuge, and elutriating the residue. Those recorded in the above table from M18 to the end were so treated. The clay was obtained by difference. The results still were unsatisfactory. These elutriations were carried on for 18 to 24 hours, settling for 3 to 6 hours.

To further test the apparatus, three tests were run of 20 grams each with the following results:

SAMPLE	Can No. I.	Can. No. II	Can No. III
Mixture of Perrines, Gray and Buff	10.05	9.09	14.22
	9.46	0.57	3.36
	5.78	1.22	4.88

Three more tests of 5 grams samples were run, using the same clay:

Can No. I	Can No. II	Can No. III
10.25	0.82	4.82
4.95	0.82	6.54
3.48	14.50	5.08
*9.02	6.55	8.04

The sample marked * was run for 48 hours at half speed and for 5 hours at full speed.

In order to use a homogeneous material, two 20-gram samples of flint were run with the following results:

Can No. I	Can No. II	Can No. III
..73	4.60	12.65
4.40	5.77	11.75

Believing that one of the causes of the uncertain results was due to eddies, discs of wire gauze were put into

the funnels of the cans and three samples of the same clay were run. The results were not encouraging:

Can No. I	Can No. II	Can No. III
27.36	9.31	6.91
10.36	12.57	14.81
10.33	12.65	17.26

In order to determine whether the height of the cans would influence the accuracy of the separation a set of cans having the same diameter but double the height were made up in tin. A five-gram sample of clay was introduced after having been thoroughly slaked and agitated and having been centrifuged to remove most of the clay size particles.

The following are the results with Cutter's Sandy Clay, the cans having a thin coating of asphaltum varnish. After running two samples the interior of the cans was coated with shellac:

Clay	Rock Dust	Silt	Sand
61.32	7.21	4.78	26.69
61.58	8.21	4.28	25.93
61.12	3.27	6.68	28.93
55.44	5.84	12.81	25.91
54.77	1.42	4.56	39.25
59.24	7.09	7.93	25.74
56.14	6.45	5.28	32.13
48.71	6.21	5.65	39.43
59.41	7.11	10.38	23.10

Raritan Mining Co. Clay No. 64

Clay	Rock Dust	Silt	Sand
68.97	5.61	8.66	16.76
71.18	9.51	9.16	10.15
74.59	9.01	7.10	9.30

Mechanical analyses—Using distilled water.

The samples were centrifuged and run in the Schultze apparatus as previously described, but about two gallons of distilled water were run through at the finish. Total time of run three days.

Cutter's Sandy, five gram sample:

Clay	Rock Dust	Silt	Sand
*61.19	8.83	5.01	24.97
*54.29	8.28	12.80	24.63

Kohl-Hepp Clay. (Micaceous.)

*74.40	10.32	7.95	7.33
*52.40	20.73	7.47	19.20

*By difference.

Experiments were next tried with the electric centrifuge apparatus, such as used by the U. S. Department of Agriculture (Bureau of Soils, Bulletin No. 24) but the available speeds were found too high for the desired separations. A comparison of the following tables will show that the Department of Agriculture Soil Chemists make a wider classification of sizes than the Ceramist.

Seger		U. S. Dept. of Agric.	
Clay	0 —0.01	0.005—0.001	Clay
		0.01 —0.005	Fine Silt
Rock Dust	0.01 —0.025	0.05 —0.01	Silt
Silt	0.025—0.04	0.1 —0.05	Very fine sand
		0.25 —0.1	Fine Sand
Sand	0.04 —0.333	0.5 —0.25	Medium Sand
		1.0 —0.5	Coarse Sand

A four-tube hand centrifuge was then tried. This is geared 1:10 and one may get a speed of 600 revolutions per minute without difficulty. Five gram samples of clay were put into a tube with 50cc. of water and 10 drops of ammonia and the tube shaken by hand for 10 minutes. The tubes were put into the centrifuge and whirled at varying speeds and the particles still in suspension were examined under the microscope. Thus the proper speed was found which would precipitate all particles larger than 0.01 mm. In order to separate the fine particles thrown down by the whirling, the following method was tried. Five grams were prepared and whirled as described (300 revolutions per minute). The clay portion in suspension after whirling was decanted and the residue in the tube was again shaken with water, centrifuged and the water with suspended matter decanted. This was repeated three times and all three water separations collected, evaporated to dryness and weighed, the process was repeated twice more and the separate decantations poured into separate beakers, dried and weighed, giving results as follows:

Two samples of the same clay,

	A.	B.
First three separations	52.98	52.47
Fourth	1.55	1.73
Fifth	0.46	0.54
Residue	44.31	44.34

In the following analyses of two samples of the same clay the operation was repeated eight times.

	%	%
First six separations	53.40	53.87
Seventh separation	0.48	0.48
Eighth separation	0.80	0.74
Residue separation	44.44	44.57

Also using a clay high in clay substance:

	%	%	%
First six separations	92.22	92.59	93.00
Seventh separation	0.43	0.26	0.56
Eighth separation	0.43	0.42	0.40
Residue separation	5.81	5.50	5.44

Another clay:

	%	%
First six separations	55.56	56.00
Seventh separation	0.64	0.50
Eighth separation	0.60	0.44
Residue separation	42.30	42.33

Our later experience has indicated that 10 to 12 separations still furnish some matter in suspension.

After separating the clay size particles, the residue was separated into its various sizes, following the Seger classification, by means of the subsidence method. Examination with the microscope of a drop of water taken from above the settled portion enabled us to determine the time necessary for the settling out of particles exceeding the desired size. This shaking, decanting and settling is repeated for each definite settling period until the supernatant fluid is cleared of all except an opalescence. The operation is repeated for the separation of each size, the settling period becoming shorter with increasing size of particle.

The time for making an analysis by this method is about three hours for continuous attention to the operation. After that about twelve hours are needed for the evaporations, which however, require little time or attention from the operator. Amount of water required is

about a liter for the separation of the clay, a liter for the separation of the rock dust, about 700 cc. for the silt, and for the sand only enough for washing the portion into the beaker for drying. Two samples in duplicate or four single samples may be run at the same time.

For the purpose of comparison, samples of the same clay were centrifuged to remove the clay size particles and the residue was run in a Hilgard elutriator, with the following results:

Sand	Silt	Rock Dust	Clay (by difference)
24.39	2.65	7.80	65.16
22.56	6.10	6.66	64.68
26.80	3.68	7.58	61.94
27.77	2.69	7.65	61.89

The same clay was elutriated in Schoene apparatus, after the clay size particles had been removed by the centrifuge.

Sand	Silt	Rock Dust	Clay (by difference)
26.89	5.11	8.61	59.39
28.12	6.59	8.28	57.01

The preliminary removal of the clay size was not contemplated by the authors of the above methods and confers upon them a distinct advantage which however does not appear in the results.

The same clay analysed by the centrifuge and subsidence method gave:—

Sand	Silt	Rock Dust	Clay (by difference)
24.20	8.21	6.70	59.78
24.15	7.72	6.74	60.37

Analysed by the Schultze method:—

Sand	Silt	Rock Dust	Clay (by difference)
24.36	0.60	3.54	71.50
23.19	0.97	1.99	73.85

It will be noted that we have not prepared our samples by boiling but have followed the method recommended by Schloesing, namely, adding a few drops of ammonia water. This is the practice of the soil chemists of the U. S. Agricultural Department. Osborne objects to boiling for the reason that it might cause dehydration and change of physical properties known to occur in the case of many colloids, also likely to cause abrasion and reduction of the coarser sediments and dehydration and coagulation of the true clays. We did not find flocculations in any samples examined under the microscope, excepting in the case of one sample of flint, and probably the use of ammonia gave us the freedom. It has been found (U. S. Dept. of Agric., Bureau of Soils, Bulletin No. 24) "that in strongly alkaline soils containing more than 1% soluble matter, the addition of ammonia has either little effect or the use has actually diminished the clay content." Since it is known that the presence of alcohol lessens the tendency to flocculation and having in mind the observation of Mellor and his associates (Studies on

Clay Slip, *Trans. Eng. Cer. Soc. Pt. II, p. 68*) that alcohol has no appreciable effect upon the slip while ammonia salts do, it seems that ammonia should not be used but alcohol should be substituted. This observation is made, however, without the support of experiment by the authors.

The water used in the experiments, excepting distilled, was the ordinary city supply filtered as described. It is a soft, ground water and we found it to contain

60 pts. per million of solids upon evaporation and

42 pts. per million of solid after ignition, which may be compared with standards as given by Nason, namely:—

29.5 for rain water

96.7 for upland surface water (Nason, "Examination of Water," p. 21, 1899).

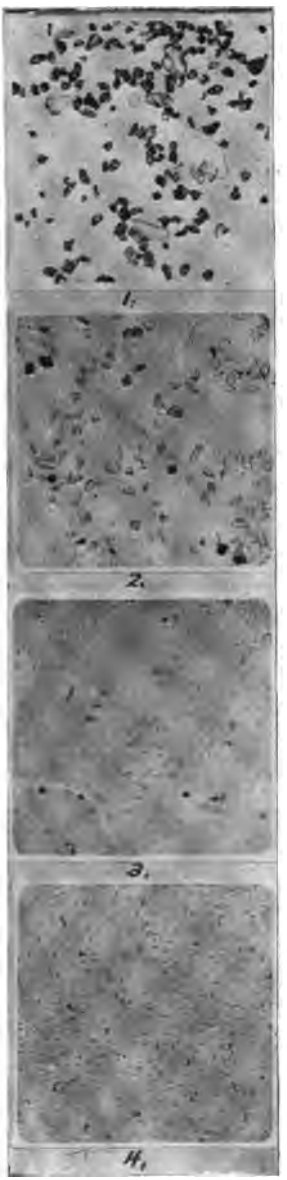
Regarding the various classifications of sizes of particles and their nomenclature, we have already given a table. Some standard should be settled upon by the ceramic chemist. Seger's classification has the advantages of being simpler and also it is arranged according to properties which are of importance from the ceramic point of view. For example, he called that portion from 0—0.01 clay size, because it shows a characteristically clay plasticity. The portion between 0.01 and 0.025 he groups together because this portion has a certain plastic coherency while wet. The soil chemist designates as clay, that portion between 0 and 0.005 and as silt the particles between 0.05 and 0.005. It would appear to the writers that the Seger classification should be retained, excepting as the importance of separating the colloidal clay may become evident.

In conclusion we wish to sum up our observations as follows:—

These opinions are based upon the conduct of one type, i. e., plastic non-calcareous clays and our conclusions relate to them only.

The centrifugal subsidence method is accurate, quick and easily manipulated. It permits the retention and weighing of all residues without requiring the use of an excessive amount of water. The hand centrifuge is cheap. A microscope is a desirable but not indispensable accessory since the centrifuge may be standardized to the work.

The Schultze method is not accurate, neither are the Schoene nor Hilgard and further the latter are expensive, troublesome, fragile, time-consuming, requiring much water and in operation losing by washing away all the clay size, thus preventing check weighings.



Centrifugal Apparatus.

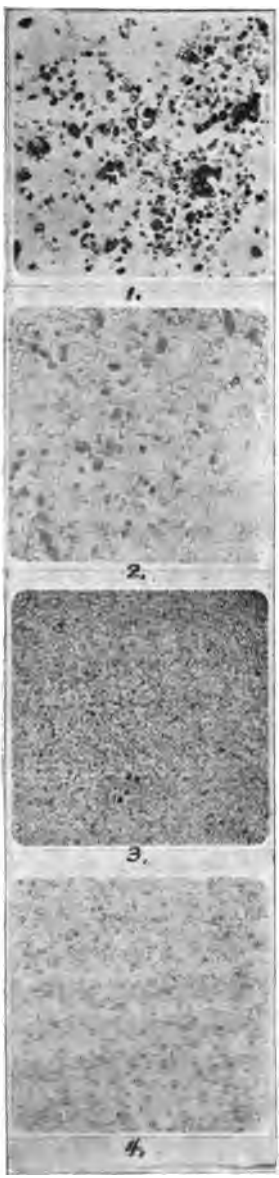
CUTTER'S SANDY CLAY.

1.
SAND.
0.04 mm diameter and greater.
Mag. X 16.

2.
SILT.
0.025 to 0.04 mm diameter.
Mag. X 50.

3.
ROCK DUST.
0.01 to 0.025 mm diameter.
Mag. X 50.

4.
CLAY SUBSTANCE.
0 to 0.01 diameter.
Mag. X 140.



Centrifugal Apparatus.

GROUND FLINT.

1.
SAND.
0.04 mm diameter and greater.
Mag. X 16.

2.
SILT.
0.025 to 0.04 mm diameter.
Mag. X 50.

3.
ROCK DUST.
0.01 to 0.025 mm diameter.
Mag. 50.

4.
CLAY SUBSTANCE.
0 to 0.01 mm diameter.
Mag. X 140.

Schoene Apparatus.

CUTTER'S SANDY CLAY.

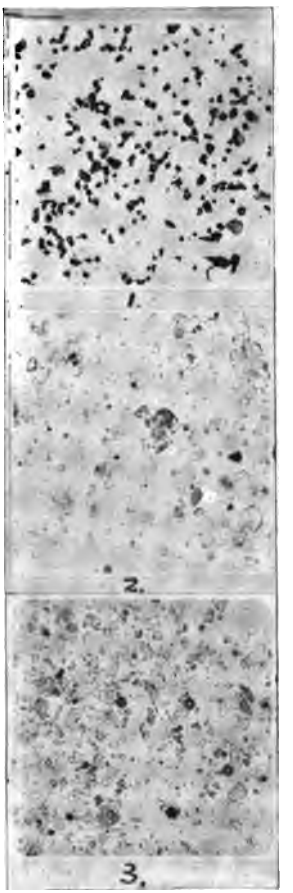
1.
SAND.
0.04 mm diameter and greater.
Mag. X 16.

2.
SILT.
0.025 to 0.04 diameter.
Mag. X 50.

3.
ROCK DUST.
0.01 to 0.025 mm
Mag. 50.

Schultze Apparatus.

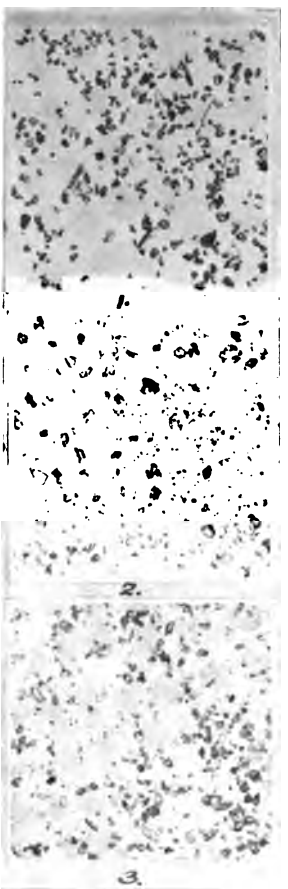
CUTTER'S SANDY CLAY.



1.
SAND.
0.04 mm diameter and greater.
Mag. X 16.

2.
SILT.
0.025 to 0.04 mm diameter.
Mag. X 50.

3.
ROCK DUST.
0.01 to 0.025 mm diameter.
Mag. X 50.



Schultze Apparatus.

CUTTER'S SANDY CLAY.

1.
SAND.
0.04 mm diameter and greater.
Mag. X 16.

2
SILT.
0.025 to 0.04 mm diameter.
Mag. X 50.

3
ROCK DUST.
0.01 to 0.025 mm.
Mag. X 50.

DISCUSSION.

Dr. Ries: I would like to ask if these photographs all represent the same degree of magnification?

Mr. Parmelee: No; that is indicated on the margins. It is manifestly impossible to do that.

I would like to have the members inspect the different prints so as to compare the methods as to accuracy in separation.

Mr. Ashley: I have performed in the last year approximately 200 elutriations with the Schultze apparatus. I believe I encountered all the difficulties Mr. Parmelee enumerated and overcame a portion of them. As to degree of accuracy, I am unable to compare directly with his results for the reason that I used the Jackson-Purdy surface factor as a means of comparing results. In that we get a number proportional to the total area of the grains in a unit weight of clay. I performed one elutriation upon a sample of clay which I called standard, using it for comparisons from time to time to check the regularity or uniformity of my operations. I sent some of it to Prof. Binns for checking, and I believe his surface factor was 143 and mine 146. I believe he said his students in their work usually checked each other closer than three or four per cent on the surface factor.

The Chair: What surface factor do you use?

Mr. Binns: We use the Jackson-Purdy factor.

Mr. Ashley: (Making drawing on board) In operating the Schultze apparatus, I think I can show the principal difficulty encountered and how it was overcome. In the first place, the clay slip is charged thru the funnel into the small can, flowing to the bottom, then rising slowly, overflowing into the funnel in the top of the second can, and so on into the third can. Now, I found this clay slip has, apparently, viscocity greater than water, or possibly I should say, specific gravity greater than that of the clear water. As the slip goes out of the first can, it is followed and replaced underneath by water. Suppose the water comes up to this level (indicating), and the slip above has greater specific gravity than the water below, the clay slip tends to fall in masses; in other words, there are eddy currents. Some clay is carried up in the clear water currents at a speed greater than that at which the can was designed to operate. I successfully overcame this by starting the run at a velocity of half (or one third) of normal velocity; so that the eddy currents approximated the correct speed of operation. When the water

in the second can ceased to be very turbid, I brought the speed up to normal, 100cc. in 34 seconds.

Another difficulty which was comparatively inconsiderable was that the sixty degree angle of the cone at the bottom of the can allowed some material to lodge on it; and in the apparatus which I have since constructed I have a somewhat sharper angle, a thirty-degree angle in the first two cans. The lodging did not seem to occur to the same degree in the third can, so the sixty-degree cone was retained in that. I boiled the slip for perhaps a minute with constant stirring with a thick glass rod until I had apparently a nearly uniform slip; then I put it into a bottle in which it was shaken for at least an hour before the run was commenced. Under those conditions I believe we got a mechanical subdivision which may be very closely compared with what is obtained in a blunger in pottery working; but I do not believe I got the ultimate size of particles. There is still a certain degree of fluctuation. But I think the results we got are close to the condition of slip used in pottery work.

Member: You used no ammonia in the precipitation?

Mr. Ashley: None whatever.

Mr. Parmelee: As I said, from this point down (indicating on chart) the clay size particles were previously taken out by centrifuge: why is it, Mr. Ashley, that we still had trouble? We tried practically the method you suggest, starting with a slow speed, and we still continued to find inaccuracies — not constant inaccuracies.

Mr. Ashley: There was one other difficulty which we encountered, namely, change of temperature in the water with which elutriation takes place. I would get the water carefully to running at a certain temperature, leave it, and when I would come back would find it running with perhaps ten per cent greater velocity, the supply in the pipe having warmed up in my absence. So a source of water supply at a constant temperature is quite necessary in operating the Schultze apparatus.

Mr. Parmelee: Do you have a constant level?

Mr. Ashley: I had very frequently to alter that to accommodate varying temperatures in the water supply.

Mr. Parmelee: We checked up on the flow frequently but did not meet with such a condition as that, tho I cannot say we looked for it.

Mr. Binns: I regret that I was not here when the paper was being read. The sketch which Mr. Ashley has put on the board seems identical with the apparatus which we are using, tho it was designed without knowing of the Schultze apparatus. It was designed at the time, not for clay, but for the separation of fine grains of flint and spar. We have very rarely used it for clay and it is undoubtedly open to the objections made. In its use on finely ground flint and spar it produced excellent results. The results have been commensurate, concordant, and accurate and have given us valuable information as to the different degrees of fineness.

Were the two samples the same flint?

Mr. Parmelee: Yes, sir; the same flint: We had it in a bottle from which we could take samples at any time.

Mr. Binns: I have not found any such discrepancies as those.

Mr. Bleininger: I do not think I can add anything to what has been said on this topic. My experience with this apparatus has been quite limited. We made, last summer, something like sixty or seventy determinations of clays of quite a sandy character; but in this we did not work for accuracy so much as to obtain the quantity of particles exceeding a certain size, since the work was done for determining the suitability of clay for cement purposes. Our experience has been practically that of Mr. Ashley. I know we had considerable trouble as to the temperature effect, in regulating the flow of water. We accomplished our purpose but were not able to check ourselves very closely. I am sorry I haven't any figures here.

Mr. Purdy: Why is it, after removing those finest particles, which he has designated as clay particles, he still had difficulty in checking — could not check any better after removing the fine particles than before?

Mr. Ries: You mean with the Schultze apparatus?— I do not know as I could say. I have never worked with that apparatus myself. I have worked mostly with the centrifugal apparatus and gotten fairly good results with that.

Mr. Purdy: Fairly good results are recorded here. Professor Binns, have you any theory as to this big discrepancy? Why are these figures of the Schultze so low as compared with the others?

Mr. Binns: Are those supposed to be the same conditions?

Mr. Purdy: Supposed to be the same clay, is it not?

Mr. Parmelee: Yes, sir.

Mr. Binns: How were the sizes determined — by microscopic measurement?

Mr. Parmelee: Yes, sir; measured by the microscope. That is, the speed of the Schultze apparatus was determined by an examination of the particles coming over, just as with the Schoene and Hilgard. In the case of centrifuge, we took a drop of the liquid with the suspended particles and examined that, of course.

Mr. Binns: I am unable to explain it, Mr. President.

Mr. Parmelee: Perhaps this explanation offered by an agricultural chemist may account for some of this irregularity. He says a flat plate will have a different rate of fall than one on edge.

Mr. Purdy: How many flat plates did you have — few and far between, were they not?

Mr. Parmelee: No, I don't think so. It is pretty hard to answer that. There were some mineral forms there which were flat and some apparently not flat.

Mr. Ashley: In the sample of clay which was elutriated by Professor Binns and myself I feel positive there were a large proportion of grains which were fairly

flat. It was a sample of North Carolina china clay and the residues obtained had a silky appearance, so it was nearly crystalline.

Mr. Purdy: That plate structure did not interfere with your checking?

Mr. Parmelee: No. We did not get as close check as we wished, but it was satisfactory for our purposes.

Mr. Purdy: How did the results check with the centrifuge? Within one per cent?

Mr. Parmelee: Usually, yes.

Mr. Purdy: Why did you call this "sand" and that "clay"? Because someone else did?

Mr. Parmelee: Yes; this classification is based on Seger's, based on the size of the particles.

Mr. Purdy: Do you think that is sand?

Mr. Parmelee: Well, what is sand?

Mr. Purdy: You may be correct in classifying coarse particles as sand, but is a clay sandy because it is coarse? My contention is that materials are ill-named if called "silt", "clay", "sand", etc., simply because the sizes of their grains fall within certain range.

Mr. Ries: My only reason for making my classification was because the Agricultural Department did. The reason was, I suppose, that they could get a finer separation with that machine.

THE COMPARATIVE EFFECTS OF THE OXIDES OF CALCIUM, MAGNESIUM, STRONTIUM, BARIUM AND ZINC ON SOME CHINA BODIES.

BY

HEREFORD HOPE, Beaver Falls, Pa.

OBJECT OF THE WORK.

The object of this investigation was to determine the effect of these oxides on some of the physical properties of various bodies consisting of flint, feldspar and clay only. The special properties on the basis of which the examinations were made were those of toughness, shrinkage, porosity, color, tendency to blister, and, in a very general way, of translucency.

SCOPE OF THE WORK.

Three mixtures containing respectively 10%, 15% and 20% of feldspar were taken and to each was added the following proportions of each of the five fluxes: .01, .03, .05, .1, .2, .3 and .5, equivalents. The majority of the trials were fired at cone 9, though several sets were fired at 10 also.

MATERIALS USED.

Flint.—Sand flint from Wedron, Ill., ground 8 hours by Ohio Silica Co., East Liverpool, O.

Feldspar.—Canadian feldspar from the Pennsylvania Feldspar Co., Philadelphia, Pa.

China Clay.—MGR brand (known also as CD), English, imported by Moore & Munger of New York.

Ball Clay.—No. 1 Grey Plastic Tenn. Ball Clay from the Mandle-Sant Clay Co., St. Louis, Mo.

Fluxes.

Whiting.—English Cliffstone Paris White, imported by the American Whiting & Putty Mfg. Co.

Magnesite.—Grecian, imported and ground by Hammill & Gillespie, New York.

Strontium Carbonate.—Pure grade, obtained from E. H. Sargent & Co., Chicago, Ill.

Barium Carbonate.—Precipitated, from Gabriel & Schall, New York.

Zinc Oxide.—Best grade, from the Roessler & Hasslacher Chemical Co.

The analyses of these materials are as follows:

	Feldspar	Tenn. Ball Clay	MGR China Clay
Loss on ignition	.004	13.94	12.16
SiO_2	62.500	47.26	46.87
Al_2O_3	24.300	35.85	38.27
Fe_2O_3	.....	1.01	.42
CaO	.760	.58	.15
MgO	.....	.68	.06
K_2O	8.754	.74	1.80
Na_2O	3.854	.45	.49
	100.172	100.51	100.92

	Whiting	Magnesite
Moisture	0.01	0.19
SiO_2	1.06	1.46
Al_2O_3	1.28	Tr.
Fe_2O_3	Tr.	Tr.
$CaCO_3$	97.20	10.50
$MgCO_3$	0.61	87.28
	100.16	99.43

Flint, Strontium Carbonate, Barium Carbonate and Zinc Oxide were considered pure.

METHOD OF PROCEDURE.

The formulae of the three bodies taken were calculated from the analyses, as were also their combining weights, the latter determining the percentage weights corresponding to the various equivalents of each flux. The clay used in each body was in the proportion of 2/3 china to 1/3 ball.

The following tables give the percentage weights of each flux added:

Molecular weights of the fluxes used:

Calcium Carbonate (Whiting	100
Magnesium Carbonate (Magnesite)	84
Strontium Carbonate	147
Barium Carbonate	197
Zinc Oxide	81

BODY 1 (Combining Weight 586.5).

Batch Weights.			*Formula.*		
Feldspar	10.0%				
China Clay	26.7 }	40%	.141 KNaO }	1.000 Al_2O_3	: 7.347 SiO_2
Ball Clay	13.3 }		.035 CaMgO }		
Flint	50.0				
	100.0%				

Percentages by weight of fluxes to add to above batch weights:

Indicating Letter	Equivalents Added	Ca Series ($CaCO_3$)	Mg Series ($MgCO_3$)	Sr. Series ($SrCO_3$)
.....	.....	.....	a	0.00
b	0.01	0.17%	0.14%	0.25
c	0.03	0.51	0.43	0.75
d	0.05	0.85	0.72	1.25
e	0.1	1.70	1.43	2.50
f	0.2	3.41	2.86	5.01
g	0.3	5.11	4.30	7.52
h	0.5	8.53	7.17	12.53

Indicating Letter	Equivalents Added	Ba Series ($BaCO_3$)	Zn Series (ZuO)
a	0.00	.....	.....
b	0.01	0.34	0.138
c	0.03	1.01	1.41
d	0.05	1.68	0.69
e	0.1	3.36	1.38
f	0.2	6.72	2.76
g	0.3	10.08	4.14
h	0.5	16.79	6.91

Body 2 (Combining Weight 517).

Batch Weights.			*Formula.*		
Feldspar	20.0%				
China Clay	26.7	40%	.207 KNaO .041 CaMgO	1.000 Al_2O_3	: 6.149 SiO_2
Ball Clay	13.3				
Flint	40.0				
	100.0%				

Percentages by weights of fluxes to add to above batch weights:

Indicating Letter	Equivalents Added	Ca Series ($CaCO_3$)	Mg Series ($MgCO_3$)
a	0.00	.....	.....
b	0.01	0.19	0.16
c	0.03	0.58	0.49
d	0.05	0.97	0.81
e	0.1	1.93	1.62
f	0.2	3.86	3.25
g	0.3	5.80	4.87
h	0.5	9.67	8.12

Indicating Letter	Equivalents Added	Sr. Series ($SrCO_3$)	Ba Series ($BaCO_3$)	Zn Series (ZnO)
a	0.00	.....	.....	.....
b	0.01	0.28	0.38	0.16
c	0.03	0.85	1.14	0.47
d	0.05	1.42	1.90	0.78
e	0.1	2.84	3.81	1.57
f	0.2	5.69	7.62	3.14
g	0.3	8.53	11.43	4.70
h	0.5	14.21	19.05	7.83

BODY 9 (Combining Weight 455.8).

Batch Weights.			*Formula.*		
Feldspar	15.0%				
China Clay	33.3 }	50%	.160 KNaO }	1.000 Al_2O_3	: 5.160 SiO_2
Ball Clay	16.7 }		.032 CaMgO }		
Flint	35.0				
	100.0%				

Percentages by weight of fluxes to add to above batch weights:

Indicating Letter	Equivalents Added	Ca Series ($CaCO_3$)	Mg Series ($MgCO_3$)
a	0.00	.....	.....
b	0.01	0.22	0.18
c	0.03	0.66	0.55
d	0.05	1.10	0.92
e	0.1	2.19	1.84
f	0.2	4.38	3.68
g	0.3	6.57	5.52
h	0.5	10.97	9.21

Indicating Letter	Equivalents Added	Sr. Series ($SrCO_3$)	Ba Series ($BaCO_3$)	Zn Series (ZnO)
a	0.00	.....	.....	.....
b	0.01	0.32	0.43	0.18
c	0.03	0.96	1.30	0.53
d	0.05	1.61	2.16	0.89
e	0.1	3.22	4.32	1.77
f	0.2	6.44	8.64	3.55
g	0.3	9.66	12.96	5.33
h	0.5	16.13	21.61	8.88

Thus there were three original body mixtures, in each of which were 5 series, 7 members to a series, making 105 bodies, or with "a" (the original body with no flux), 108 bodies altogether.

These were weighed out in batches of 2000 grams each, mixed for one hour on a small ball mill, lawned through a 120 mesh sieve and dried in plaster moulds, care being taken that the least possible surface of the clay should be in contact with the mould.

The trial pieces consisted of cubes of about 1″ face for the rattler test for toughness; bars about 3/8″ square by 2½″ long for porosity and shrinkage tests; and flat discs about 3/16″ thick and 4″ diameter for color comparisons.

The bodies were thoroughly wedged by hand, the cubes being made by pressing the plastic clay into a rectangular copper frame 3″ x 5″ and the bars made in the same manner from a frame 1½″ x 2½″. These blocks of clay, when sufficiently stiff, were cut with a knife, the large frame making 15 cubes and the small one 5 bars.

The discs were made by hand in plaster moulds.

When thoroughly dry, the bars were carefully marked, by means of a gauge, with two scratches exactly 50 mm. apart for the shrinkage measurement. The trials were marked with figures and letters, the figures representing the original body number, the middle letters the series, and the final letter the number of equivalents used. Thus 2 Mg e is the mixture of Body 2, Magnesia series and with 0.1 equivalents of MgO added.

FIRING THE TRIALS.

This was not done all at one time, but in a number of different kilns in order to obtain as complete an average of conditions as possible at the same temperature, the following being a record of the various firings:

Cone 9.

1st Firing: Result doubtful, as sand prevented cones falling. Trials thrown out.

2nd Firing: Cone 9 down, 10 started, 1st ring over bag. Earthenware biscuit kiln.

3rd Firing: Cone 9 down, 10 started, 3rd ring china kiln, regular cooling.

4th Firing: Cone 9 down, 10 slightly started, forebung china kiln; cooled slowly.

5th Firing: Cone 9 down, 10 started, 2nd ring china kiln; cooled slowly.

6th Firing: Cone 9 down, 10 started, forebung china kiln; cooled slowly.

7th Firing: Cone 9 down, 10 started, 2nd ring china kiln; cooled slowly.

8th Firing: Cone 9 down, 10 bent half over. Trials all thrown out.

Cone 10.

1st Firing: Cone 10 just down, 11 straight, 1st ring over bag. China biscuit.

On account of errors in firing, between 400 and 600 trial pieces were thrown out.

METHODS OF TESTING.

Rattler Test. After weighing, about 35 cubes were placed in a porcelain-lined ball mill $8\frac{1}{2}''$ long by $9\frac{3}{4}''$ diameter, inside measurement, with 5 lbs. of Greenland pebbles (averaging 8 or 9 to the pound) and run for 2 hours at a speed of 80 R. P. M. In two cases only did the speed run above 82 or below 78, and this was allowed for by a difference in the time of rattling. By the use of a considerable number of cubes and a comparatively small quantity of stones, it was intended to substitute for the abrasive action, something more nearly approaching a chipping effect, which was considered to be a more practical test for the bodies that might ultimately be used in the manufacture of hotel china.

Porosity.—After weighing, the bars were soaked in distilled water for 48 hours, boiled for 1 hour, and then placed under a suction pump exactly in the same manner as described by Bleininger & Moore in Vol. X *Trans. Am. Cer. Soc.* p. 302. The exhaustion was continued till no more air bubbles were seen to rise from the bars.

The pieces were weighed immediately on removal from the water, (the superfluous moisture only being taken off) giving the wet weight, and then again weighed suspended in water, thus furnishing, with the dry weight previously obtained, the factors for figuring the percentage porosity by the Purdy formula $\%P = \left(\frac{W-D}{W-S}\right) 100$, where

P=porosity.

W=wet weight of bar.

D=dry weight of bar.

S=suspended weight of bar.

Shrinkage.—50 mm. having been accurately marked off on the bars before firing as previously described, the measurement was again made after firing and the second reading taken by means of a millimeter scale. It was possible to obtain the shrinkage to 1/4 of 1%.

Color.—On account of the great variety in the shades of color of vitrified bodies, it was considered impossible to form a color scale giving absolute values; hence comparative values only are given. The discs were all glazed evenly with the same glaze (an ordinary whiteware glaze) in order to make accurate comparisons, and also to give clearer indication of the blistering of the biscuit.

RATTLER TESTS

Body I

		% Loss of Weight.							Average.
	a	3.8	3.2	4.9	6.6	4.1	3.5	4.9	4.4
Ca	b	6.8	5.4	4.6	6.0	5.9	5.8	3.9	5.5
	c	6.2	5.0	4.4	5.6	3.2	6.3		5.1
	d	5.3	4.0						4.6
	e	2.8	0.9	1.9	2.1	2.6	3.7	4.4	2.6
	f	5.8	2.3	7.4	4.2	6.0	4.2	3.4	4.8
	g	4.5	2.8	5.8	4.2	4.0	4.5	4.2	4.3
	h	4.4	4.2	5.0	2.8	2.8	4.6	3.7	3.9
Mg	b	3.8	4.6	3.7	5.2	5.1	2.7	5.7	4.4
	c	5.9	3.0	4.8	3.2	4.8	1.9	5.2	4.1
	d	4.0	1.2	4.5	3.0	1.8			2.9
	e	3.9	2.6	6.0	2.6	3.3	2.6	6.8	4.0
	f	2.8	3.4	4.3	4.3	3.4	2.0		3.4
	g	5.1	2.1	2.5	5.1		4.9	3.6	3.9
	h	3.6	2.4	3.0	2.9	5.5	3.0	4.0	3.5
Sr	b	4.2	5.3	4.8	5.4	4.3	3.7	2.8	4.4
	c	3.2	3.0	3.4	3.7	2.0 2.4	3.3	5.5	3.3
	d	3.9	0.5	2.1	1.5	1.0 1.1	1.2	0.5	3.3	1.7
	e	1.7	3.9	2.8	3.0	3.5 0.2		5.0	4.9	3.1
	f	4.7	3.0	3.2	5.9	1.6	1.4	2.5	3.2
	g	4.3	7.5	5.0	3.7	2.6	0.9	3.7	4.0
	h	7.7	12.2	8.5	6.4	5.1	6.3	6.2	7.5
Ba	b	4.1	3.3	7.2	3.3	3.8	7.7		4.9
	c	4.5	3.5	6.6	4.4	4.9	3.4	3.9	4.5
	d	5.3	2.3	5.7	5.3	3.9	3.8	3.7	4.3
	e	6.9	3.2	4.4	5.7	5.0	2.1	2.9	4.3
	f	7.0	3.4	4.9	5.5	4.8	4.0	3.1	4.7
	g	5.4	3.5	2.4	5.3	5.0	4.3	3.1	4.1
	h	6.2	8.1	7.1	4.1	3.4	2.8	3.3	5.0
Zn	b	4.2	3.3	4.9	5.7	5.6			4.7
	c	4.9	3.5	4.3	4.0	2.1	4.8		3.9
	d	3.9	5.2	4.1	2.1	5.0	4.9		4.2
	e	4.8	4.3	5.1	3.9	5.0			4.6
	f	4.3	4.4	2.5	5.2				4.1
	g	4.4	6.2	8.1	5.2				6.0
	h	2.3	4.2	5.1	3.8	3.5	5.2		4.0

RATTLER TESTS (Continued)

Body 2

		% Loss of Weight.							Average.
	a	3.9	8.6	3.7	6.4	5.5	3.3		5.2
Ca	b	5.4	4.0	1.5	9.6	5.5	4.9	3.9	5.0
	c	6.0	4.2	5.8	4.0	6.6	6.1	5.5	5.5
	d	3.4	4.6	3.6	5.3	4.4	5.7	4.1	4.4
	e	5.7	3.6	4.4	4.2	4.1	6.9		4.8
	f	5.7	4.8	5.5	4.4	3.7	8.2	7.2	4.4
	g	4.7	5.1	5.7	5.9	3.4	5.3	10.3	5.8
	h	4.7	4.7	6.5	3.6	3.5	8.5	3.3	5.0
Mg	b	2.9	1.2	4.0	1.9	3.6			2.7
	c	4.2	4.8	3.2	4.9	2.5	4.5	4.7	4.1
	d	4.0	3.8	3.6	9.3	6.0	4.2	3.1	4.9
	e	3.1	4.0	5.0	6.2	8.1		4.9	5.2
	f	6.0	5.2	4.2	5.0	3.4			4.8
	g	5.2	3.8	4.1	5.4	6.5		4.4	4.9
	h	4.0	4.3	5.1	5.4	4.1	7.0	6.7	5.2
Sr	b	6.1	3.9	2.2	1.5	4.9	4.5	2.6	3.7
	c	3.4	2.3	5.1	4.7	2.0	3.6	2.3 2.3	3.2
	d	3.5	6.5	1.8	4.6	2.5	2.3	1.9	3.3
	e	3.4	1.8	5.5	2.8	1.3			3.0
	f	3.4	3.7	4.8	3.8	1.7	5.2	4.3	3.8
	g	4.2	3.3	6.4	4.7	4.8	3.8		4.5
	h	4.9	7.1	5.8	2.5	3.0	4.4		4.6
Ba	b	6.5	3.1	1.9	3.8	1.4	6.1	2.2	3.6
	c	4.8	3.6	4.5	5.5	4.3	6.5	3.8	4.7
	d	4.5	3.3	3.9	5.5	6.4	3.4	6.9	4.8
	e	6.2	2.9	6.2	6.2	4.3	5.3	6.8	5.4
	f	5.3	8.1	5.6	4.7	4.3	4.1	7.3	5.6
	g	2.4	4.1	5.3	7.1	5.2	5.9	6.0	5.1
	h	2.3	2.4	1.4	2.6	3.8	3.3	3.5	2.8
Zn	b	3.3	4.4	4.5	5.2				4.3
	c	2.1	5.1	7.2	4.3	3.0	6.6	2.9	4.5
	d	5.6	3.1	5.9	1.7	2.1	4.2	2.4	3.6
	e	5.1	2.4	3.4	2.6	2.2	4.7	4.0	3.5
	f	5.9	3.6	4.3	2.5	4.6	4.3	5.8	4.4
	g	4.5	3.1	5.8	1.6	5.1	1.6	4.7	3.8
	h	4.3	3.2	4.6					4.0

RATTLER TESTS (Continued)

Body 9

		% Loss of Weight.							Average.
	a	4.4	5.3	3.7	5.4	5.5	4.5	3.7	4.6
Ca	b	4.4	6.4	5.2	5.5	7.7	8.2	6.6	6.3
	c	4.0	4.0	4.2	4.6	6.4	6.5	7.7	5.3
	d	3.6	5.7	4.5	4.8	8.1	5.3	7.1	5.6
	e	4.7	7.0	4.9	7.4	8.6	6.4	7.8	6.7
	f	5.2	7.0	4.1	6.2	8.4	8.0		6.5
	g	3.5	6.5	10.4	5.9	8.8	9.1	6.3	7.2
	h	4.6	2.1	10.5	7.6	9.2	9.3		7.2
Mg	b	3.1	5.8	3.4	3.3	7.5	5.1		4.7
	c	3.5	5.5	2.6	4.7	6.7	8.2		5.2
	d	3.5	5.3	4.5	7.5	3.5	4.1	4.7	4.7
	e	3.4	4.2						3.8
	f	4.1	5.4	5.2	5.7	6.0	5.5	10.0	6.0
	g	4.5	7.6	5.4	4.5	4.8	3.5	4.5	5.0
	h	4.0	6.5	5.7	5.4	5.6	4.6		5.3
Sr	b	4.6	6.8	4.0	6.1	6.6	5.0	3.5	5.2
	c	4.9	6.6	6.9	5.6	6.1	6.5	8.4	6.4
	d	4.5	8.7	4.3	6.6	9.0	7.5		6.8
	e	8.7	3.1	5.3	6.0	5.7			5.8
	f	4.0	6.1	3.6	4.2	7.0	6.8		5.3
	g	3.9	5.2	9.9	5.2	7.8	11.1	7.6	7.2
	h	4.9	5.3	6.1	9.3	10.5	3.0	7.7	6.7
Ba	b	3.2	7.3	3.8	5.3	7.1	7.2		5.6
	c	3.5	5.4	4.2	6.9				5.0
	d	4.4	4.9	5.5	8.9	8.3			6.4
	e	6.3	7.3	5.2	5.1	6.4	6.0	7.9	6.3
	f	3.9	6.7	4.1	5.1	6.0	6.2		5.3
	g	3.1	11.5	6.5	5.9	8.6	5.6		6.9
	h	14.5	6.3	5.8	7.2	10.4			8.8
Zn	b	7.5	3.6	4.2	3.8	6.3	4.3		4.9
	c	5.9	6.7	4.3	4.0	4.4	7.0		5.4
	d	10.4	5.1	2.8	5.8	4.5	4.5		5.5
	e	5.4	4.8	5.6	5.5	4.2			5.1
	f	5.4	2.6	2.7	2.7	4.8	4.8		3.8
	g	7.3	4.8	4.8	8.2	4.9	4.1		5.7
	h	5.5	7.5	6.9	9.6	5.2	7.7		7.1

Absorption Tests

Body I

		% Porosity				Average
	a	4.2	9.9	4.8	7.8	6.7
Ca	b	0.3	8.8	1.5	1.8	3.1
	c	1.4	M	3.5	4.3	3.1
	d	2.0	5.6	2.9	3.4	3.5
	e	1.6	0.7	1.8	2.9	1.7
	f	0.3	3.4	1.8	3.2	2.2
	g	5.0	2.8	1.5	2.9	3.1
	h	3.3	13.7	9.3	10.7	9.2
Mg	b	3.2	7.9	3.9	6.3	5.3
	c	1.7	7.2	2.4	4.1	3.8
	d	2.3	3.4	2.2	2.7	2.8
	e	2.6	2.7	2.5	2.3	2.5
	f	3.3	1.7	2.4	2.5	2.5
	g	2.9	2.7	2.6	3.0	2.8
	h	2.9	2.1	2.5	2.1	2.4
Sr	b	2.3	7.0	M	6.1	5.1
	c	2.4	6.6	4.0	4.6	4.4
	d	1.3	6.2	2.3	3.5	3.3
	e	0.0	6.7	M	3.0	3.2
	f	0.0	10.7	M	4.9	5.2
	g	2.4	23.6	15.3	20.8	15.5
	h	16.1	33.0	27.4	32.8	27.3
Ba	b	2.9	7.1	1.9		4.0
	c	1.7	7.6		5.3	4.9
	d	0.0	5.5	1.1	3.3	2.5
	e	0.0	1.6	0.4	0.0	0.5
	f	0.0	0.3	0.3	0.9	0.4
	g	0.0	1.8	0.0	2.4	1.0
	h	1.7	19.1	12.7	17.7	12.8
Zn	b	4.9		2.4		3.6
	c	4.6	5.2	3.6		4.5
	d	3.3	1.8	2.8		2.6
	e	4.0	4.8	4.3		4.4
	f	3.3	5.9	2.8		4.0
	g	6.8	7.7	3.7		6.1
	h	11.8	15.1	9.3		12.1

ABSORPTION TESTS (Continued)

Body 2

		% Porosity					Average
	a	0.6	0.6	0.0	0.0	0.0	0.2
Ca	b	0.9	0.0	0.0	0.0	0.3	0.2
	c	0.3	0.6	0.0	0.0	0.0	0.2
	d	0.6	0.0	0.0	0.3		0.2
	e	1.0	0.7	0.0			0.6
	f	0.0	0.7				0.3
	g	0.3	0.7	0.6	0.3	0.0	0.4
	h	0.6	0.0	0.0	0.0	0.0	0.1
Mg	b	0.6	1.1	0.0	0.0		0.4
	c	0.4	2.0	0.0	0.0	0.0	0.5
	d	0.9	0.3	0.0	0.6		0.4
	e	0.7	1.0	0.0	0.0	0.3	0.4
	f	2.6	0.8	0.0	0.6	0.3	0.9
	g	9.6	1.5	0.3	0.8	0.6	2.6
	h	13.6	8.2	2.6	1.4	0.7	5.3
Sr	b	0.0	0.6	0.0	0.0		0.1
	c	0.0	1.0	0.0	0.0	0.0	0.2
	d	0.9	1.3	0.3	0.0	0.0	0.5
	e	1.8	0.7	2.1			1.5
	f	0.3	1.2	0.0	0.0	0.0	0.3
	g	0.3	4.0	0.0	0.0		1.1
	h	1.1	19.3	2.9	2.6	3.0	5.8
Ba	b	1.2	0.7	0.0	0.0	0.0	0.4
	c	0.9	0.3	0.0	0.0	0.0	0.2
	d	0.0	0.3	0.0	0.0	0.0	0.1
	e	0.6	0.7	0.0			0.4
	f	1.1	0.0	0.0	0.0	0.6	0.3
	g	1.4	0.7	0.0	0.0		0.5
	h	2.1	5.3	0.0	2.0	0.6	2.0
Zn	b	1.2	0.6	0.0	0.0	0.6	0.5
	c	1.2	1.1	0.3	0.0		0.6
	d	0.6	0.0	0.0	0.0	0.0	0.1
	e	0.3	0.0	0.0	0.0	0.0	0.1
	f		0.0				0.0
	g	0.7	0.4	0.0	0.0	0.0	0.2
	h	1.0	1.6	0.0	0.3	0.4	0.7

ABSORPTION TESTS (Continued)

Body 9

		% Porosity				Average
	a	0.3	4.0	0.7	3.7	2.2
Ca	b	0.0	2.2	0.3	1.5	1.0
	c	0.3	0.4	1.6	0.0	0.6
	d	0.0	1.2	0.8	0.0	0.5
	e	0.0	1.0	0.0	0.0	0.2
	f	0.0	1.9	0.3	0.6	0.7
	g	0.0	0.3	0.0	0.0	0.1
	h	0.0	9.1	1.0	0.7	2.7
Mg	b	0.0	2.7	0.6	0.4	0.9
	c	0.0	1.1	1.1	1.0	0.8
	d	0.0	0.3	0.4	0.3	0.2
	e	Ml	1.1	0.9	0.9	1.0
	f	0.0	0.6	0.7	0.3	0.4
	g	4.4	3.3	1.5	1.6	2.7
	h	6.4	1.0	0.3	0.7	2.1
Sr	b	0.0	3.3	0.0	2.3	1.4
	c		1.2	0.6	0.6	0.8
	d	0.0	0.3	0.6	0.0	0.2
	e	0.0	0.0	0.5	0.3	0.2
	f	0.0	7.1	0.0	2.9	2.5
	g	0.0	17.5	0.0	12.2	7.4
	h	7.6	32.9	9.8	31.8	20.5
Ba	b	0.0	3.0	0.0	0.0	0.7
	c	0.0	0.8	0.0	0.0	0.2
	d	0.0		1.2		0.6
	e	0.0	0.4	1.3	0.0	0.4
	f	0.0	0.0	0.0	0.0	0.0
	g	0.0	7.4	0.0	0.0	1.8
	h	1.4	28.6	0.0	24.9	13.7
Zn	b	1.1	1.3	0.4		0.9
	c	1.2	0.0	0.3		0.5
	d	0.8	0.7	1.0		0.8
	e	0.8	0.3	0.6		0.6
	f	0.0	0.0	1.0		0.3
	g	1.1	0.0	0.7		0.6
	h	0.0	2.9	0.0		1.0

Shrinkage Tests

Body I

		% Shrinkage				Average
	a	10.0	8.8	10.4	9.0	9.2
Ca	b	11.8	9.2	11.8	11.0	10.9
	c	10.4		11.0	10.2	10.5
	d	10.6	10.0	11.0	11.0	10.6
	e	10.6	10.4	11.2	11.4	10.9
	f	11.0	10.4	11.0	10.8	10.8
	g	12.0	10.4	11.0	10.6	11.0
	h	10.6	8.2	10.0	9.8	9.6
Mg	b	10.4	9.2	10.6	10.0	10.0
	c	11.4	10.4	11.4	11.0	11.0
	d	10.2	10.6	11.4	11.4	10.9
	e	11.6	11.0	12.0	11.4	11.5
	f	11.2	11.4	12.0	12.0	11.6
	g	11.0	11.0	11.6	11.0	11.1
	h	11.0	11.2	11.4	11.2	11.2
Sr	b	10.6	9.0		10.0	9.8
	c	11.2	11.0	10.8	9.8	10.7
	d	11.6	10.0	11.2	10.4	10.8
	e	11.0	10.0		10.6	10.5
	f	10.0	8.2		10.0	9.4
	g	9.2	4.8	7.2	6.2	6.8
	h	5.6	1.0	2.0	2.0	2.1
Ba	b	11.0	10.0	11.4		10.8
	c	11.0	10.2		11.4	10.8
	d	12.0	11.0	12.0		11.7
	e	11.4	11.6	12.0	12.0	11.7
	f	12.0	11.6	13.0	13.4	12.5
	g	11.8	11.8	12.6	12.4	12.1
	h	11.6	7.6	9.4	8.0	9.1
Zn	b	11.0	11.6	11.6		11.4
	c	12.0	12.0	13.0		12.3
	d	11.0	12.0	12.0		11.7
	e	11.4	12.0	12.0		11.8
	f	12.0	12.6	11.4		12.0
	g	11.0	12.0	12.4		11.8
	h	10.0	9.8	10.2		10.0

SHRINKAGE TESTS (Continued)

Body 2

		% Shrinkage					Average
	a	10.0	11.4	12.0	12.0	12.6	11.6
Ca	b	11.2	11.4	11.4	10.8	11.8	11.3
	c	12.0	11.6	12.8	12.2	12.8	12.3
	d	12.4	11.6	12.4	11.8	11.4	11.9
	e	11.0	11.6	11.8			11.5
	f	11.4	12.0				11.7
	g	12.2	11.2	11.0	11.4	10.6	11.3
	h	11.0	11.8	11.6	11.0	11.6	11.4
Mg	b	12.0	11.8	12.0	11.6	12.0	11.9
	c	10.8	11.4	10.4	10.8	11.4	11.0
	d	12.0	12.6	12.0	12.0		12.1
	e	10.2	11.6	11.4	11.6	11.8	11.3
	f	8.8	10.0	10.0	10.0	9.0	9.6
	g	6.0	7.2	7.0	7.0	7.4	6.9
	h	6.0	9.4	6.8	7.6	8.0	7.6
Sr	b	11.8	10.8	12.6	12.0		11.8
	c	11.8	12.0	11.0	10.8	11.2	11.4
	d	12.2	12.6	11.4	12.0	11.6	12.0
	e	10.4	11.2	10.6			10.7
	f	9.8	10.8	8.8	8.6	10.0	9.6
	g		10.0	10.8			10.4
	h	7.8	5.8	8.0	8.4		7.5
Ba	b	12.4	12.0	12.0	12.0	11.8	12.0
	c	12.6	11.4	12.6	11.4		12.0
	d	12.0	11.8	11.8	11.4	11.6	11.7
	e	12.0	12.4	12.4			12.3
	f	11.0	12.4	11.0	11.6	10.4	11.3
	g	10.0	11.4	10.8	10.6		10.7
	h	10.2	9.6	10.2	9.8	9.8	9.9
Zn	b	12.6	13.0	13.0	13.4	12.4	12.9
	c	12.8	13.0	12.4	12.0	12.0	12.4
	d	12.0	14.0	12.6	12.0	13.6	12.8
	e	12.4	13.4	13.0	13.6	12.6	13.0
	f		13.0				13.0
	g	14.0	13.6	13.0	12.6	13.4	13.3
	h	13.6	14.4	13.0	12.6	13.2	13.4

SHRINKAGE TESTS (Continued)

Body 9

		% Shrinkage				Average
	a	12.6	11.6	12.0	10.8	11.7
Ca	b	12.0	11.2	11.2	10.6	11.2
	c	12.0	12.4	12.2	11.0	11.9
	d	12.6	12.0	12.6	13.0	12.5
	e	12.8	12.4	12.0	12.0	12.3
	f	13.0	12.6	12.0	11.6	12.3
	g	12.4	11.6	12.0	12.2	12.0
	h	12.4	9.2	12.0	10.4	11.0
Mg	b	12.4	12.2	12.8	11.6	12.2
	c	13.0	13.0	14.0	12.0	13.0
	d	12.0	12.8	14.2	12.6	12.9
	e	12.0	13.0	12.4	12.4	12.4
	f	10.0	12.4	11.0	12.4	11.4
	g	11.0	12.8	12.0	12.0	11.9
	h	10.2	12.4	12.0	13.0	11.9
Sr	b	12.4	11.8	13.0	11.8	12.2
	c	12.0	11.8	13.0	12.0	12.2
	d	11.0	11.6	12.0	12.0	11.6
	e	10.6	10.8	11.0	12.0	11.1
	f	11.0	9.8	11.4	10.6	10.7
	g	10.0	7.0	9.8	8.2	8.7
	h	7.0	2.0	6.8	2.4	4.5
Ba	b	12.0	11.2	13.0	12.0	12.0
	c	12.4	12.0	12.0	12.2	12.1
	d	13.0	12.2	12.6	13.0	12.7
	e	12.4	12.0	13.0	12.0	12.3
	f	12.6	12.6	12.2	14.8	13.0
	g	13.0	12.0	12.0	12.2	12.3
	h	11.8	5.6	13.4	6.4	9.3
Zn	b	12.0	13.2	13.4		12.8
	c	13.0	13.0	13.0		13.0
	d	13.8	14.0	14.0		13.9
	e	13.6	12.4	13.8		13.3
	f	12.6	13.6	13.6		13.3
	g	13.6	14.8			14.2
	h	14.0	13.0	15.0		14.0

Color Comparisons.

Body 1.

Comparison of the same equivalent of different fluxes.

.01 eqv. (b) Zn distinctly best; others equal.

.03 eqv. (c) Zn distinctly best; Mg. distinctly better than other three.

.05 eqv.(d) Zn best; Mg decidedly better than other three.

.1 eqv. (e) Mg best; Zn becoming bluish, others much inferior.

.2 eqv. (f) Mg best; Zn next; Ba worst.

.3 eqv. (g) Mg much best; Zn next but bluish; Ba worst

.5 eqv. (h) Sr best (not vitrified); Ca next; Mg next (darkening); Zn bluish.

Comparison of different members of each series.

Ca. Very little change in color throughout series.

Mg. Decided improvement as far as .2 eq. (f); then becomes darker.

Sr. Very little change in color throughout series.

Ba. Very little change in color throughout series.

Zn. Decided improvement as far as .05 eq. (d), then becoming bluish.

Body 2.

Comparison of the same equivalents of different fluxes.

.01 eq. (b) Zn distinctly best; others equal.

.03 eq. (c) Zn best; Mg next; Sr slightly better than others.

.05 eq. (d) Mg best; Zn next; other three about equal.

.1 eq. (e) Zn much best; Mg next; Sr next; others equal.

.2 eq. (f) Zn very much best; Mg next but far inferior; Sr distinctly better than other two.

.3 eq. (g) Zn best; Mg next; Sr decidedly better than other two.

.5 eq. (h) Zn much best; Mg next; Sr decidedly better than other two.

Comparison of different members of each series.

Ca. No distinct change.

Mg. Decided improvement to .2 eqv. (f) then declines.

Sr. Distinct improvement to .3 eqv. (g) then declines.

Ba. Slight improvement at .01 eqv. (b) then darkens throughout series, especially at .05 eqv.

Zn. Very marked improvement to .2 eqv. (f) then slight decline (becoming bluish).

Body 9.

Comparison of the same equivalent of different fluxes.

.01 eqv. (b) Zn slightly better than others.

.03 eqv. (c) Zn slightly better than others.

.05 eqv. (d) Zn best but bluish; Mg next; Ca slightly better than others.

.1 eqv. (e) Zn and Mg equal; others inferior but with Ca a little better than others.

.2 eqv. (f) Mg much better than others (Zn greenish); Ba worst.

.3 eqv. (g) Zn much better than others; Mg next; Ba worst.

.5 eqv. (h) Zn much better than others; Mg darkening.

Comparison of different members of each series.

Ca. Slight improvement to between .03 eqv. (c) and .05 eqv. (d); then slightly darker.

Mg. Decided improvement to .02 eqv. (f); then darker.

Sr. Slight improvement throughout series.

Ba. Very little change throughout series.

Zn. Decided improvement, becoming bluish after .1 eqv. (e).

Comparisons for Blistering.

In looking over the glazed discs for comparative color effects, it was noted that there were great differences as regards the tendency of the glaze to pinhole; and as on closer examination this defect was found to exist in the

biscuit, the matter was considered of sufficient importance to be observed closely in order to determine if possible what effect upon this property might be attributed to the kind and quantity of the fluxes used.

The following table gives a rough comparison:

Abbreviations used: "Abs." = blistering absent; "Mod." = moderate; "V. Sl." = very slight; "excess" = excessive.

Body 1.

		Ca.	Mg.	Sr.	Ba.	Zn.
.00 eqv.	a	blistering	absent			
.01 eqv.	b	V. Sl.	Sl.	Abs.	V. Sl.	Mod.
.03 eqv.	c	Abs.	Abs.	Abs.	Sl.	Sl.
.05 eqv.	d	Abs.	Abs.	Abs.	Abs.	Sl.
.1 eqv.	e	Abs.	V. Sl.	Abs.	Mod.	Sl.toMod.
.2 eqv.	f	Abs.	Abs.	Abs.	Bad.	Sl.
.3 eqv.	g	Abs.	V. Sl.	Abs.	Mod.	V. Sl.
.5 eqv.	h	Abs.	Abs.	Abs.	Mod.	Abs.

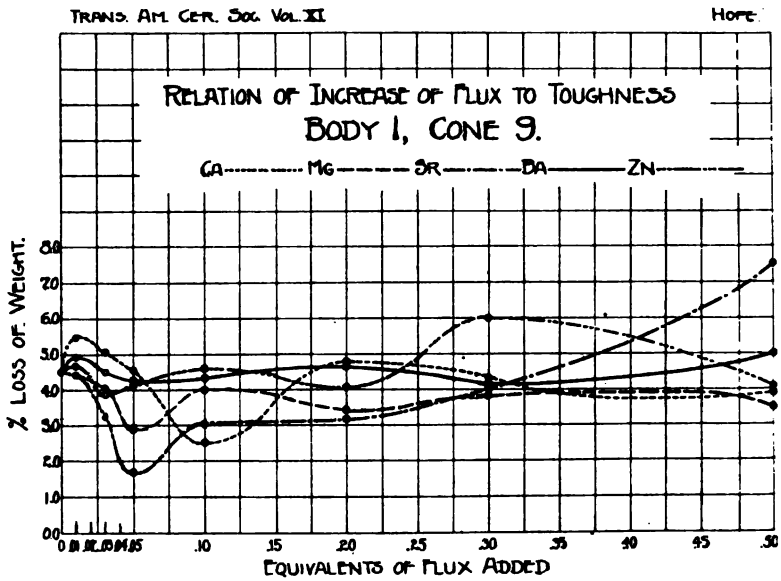
Body 2.

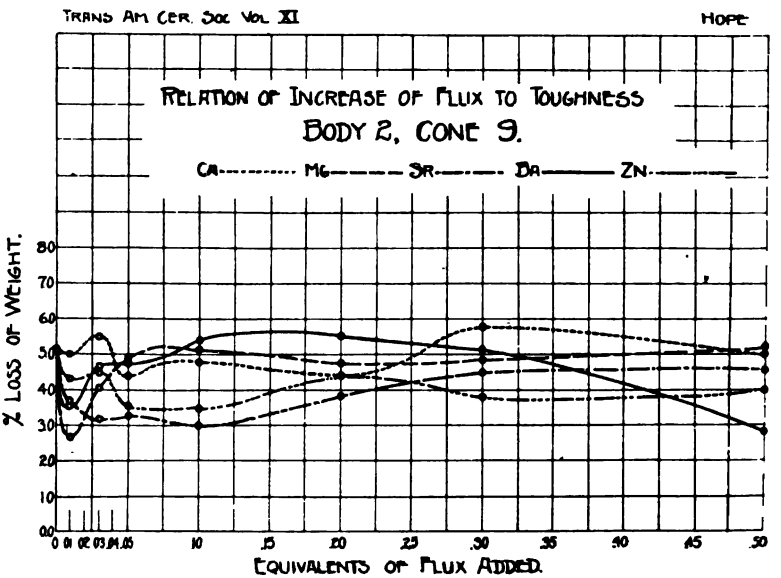
		Ca.	Mg.	Sr.	Ba.	Zn.
.00 eqv.	a	Sl.	Sl.	Sl.	Sl.	Sl.
.01 eqv.	b	V. Sl.	V. Sl.	V. Sl.	Mod.	Sl.
.03 eqv.	c	Abs.	V. Sl.	Sl.	Mod.	Sl.
.05 eqv.	d	V. Sl.	Sl.toMod.	Abs.	Sl.	V. Sl.
.1 eqv.	e	V. Sl.	V. Sl.	Sl.	Mod.-Bad	Sl.
.2 eqv.	f	V. Sl.	Bad.	V. Sl.	V. Bad.	Mod.
.3 eqv.	g	Abs.	V. Bad.	Abs.	Bad.	Mod.
.5 eqv.	h	V. Sl.	Mod.	V. Sl.	Bad.	Sl.

Body 9.

		Ca.	Mg.	Sr.	Ba.	Zn.
.00 eqv.	a	Sl.	Sl.	Sl.	Sl.	Sl.
.01 eqv.	b	Abs.	Abs.	V. Sl.	Abs.	V. Sl.
.03 eqv.	c	Abs.	V. Sl.	Abs.	V. Sl.	Sl.
.05 eqv.	d	Abs.	V. Sl.	Abs.	Abs.	V. Sl.
.1 eqv.	e	Abs.	Sl.	Abs.	Sl.	V. Sl.
.2 eqv.	f	Sl.	Bad.	V. Sl.	Bad.	V. Sl.
.3 eqv.	g	V. Sl.	Bad.	V. Sl.	Bad.	Sl.
.5 eqv.	h	Abs.	V. Sl.	Abs.	Sl.	Missing

SUMMARY OF RESULTS OF TESTS.

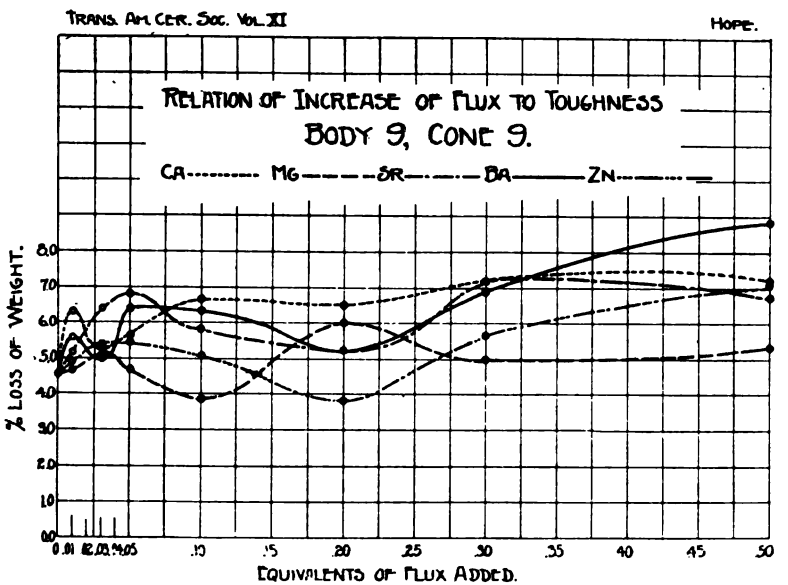




Rattler Tests. Body 1. The toughest bodies are found to be those containing an addition of from .05 to .1 eq. of flux, this being especially true of the Ca and Sr series; though in the Zn series there seems little difference between any of the members in this respect. In the Sr series, the bodies containing large percentages of the flux show a very considerable loss owing to the rapidly increasing refractoriness and consequent weakness.

Body 2. To a less marked degree than in body 1, the same remarks hold true, though in the Mg and Zn series, the toughest bodies are found at .01 eq. of flux.

Body 9. No definite conclusions can be drawn from these series, though all the bodies show less strength than body 1.

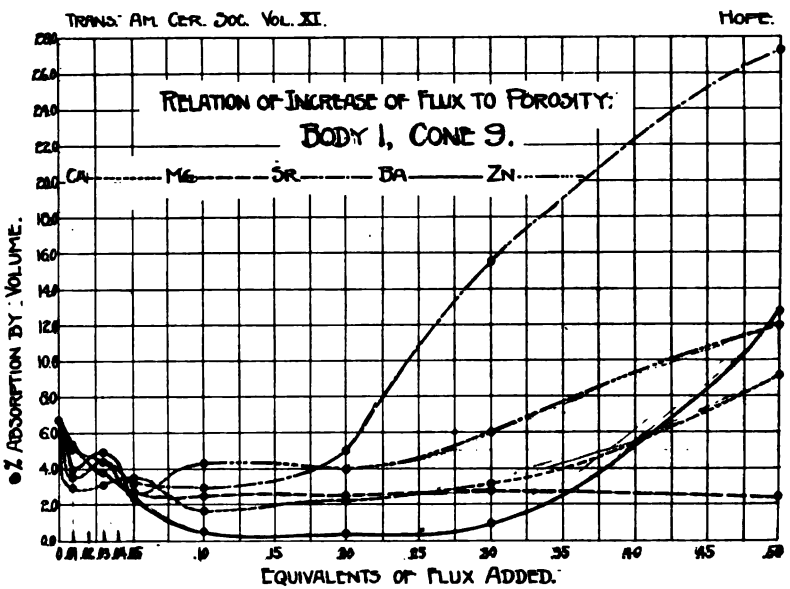


Averages by Series.

Loss of Weight %

	Body 1	Body 2	Body 9	Average
Ca	4.4	5.0	6.4	5.3
Mg	3.7	4.5	5.0	4.4
Sr	3.9	3.7	6.2	4.6
Ba	4.5	4.6	6.3	5.1
Zn	4.5	4.0	5.4	4.6
General Averages	4.2	4.4	5.9	

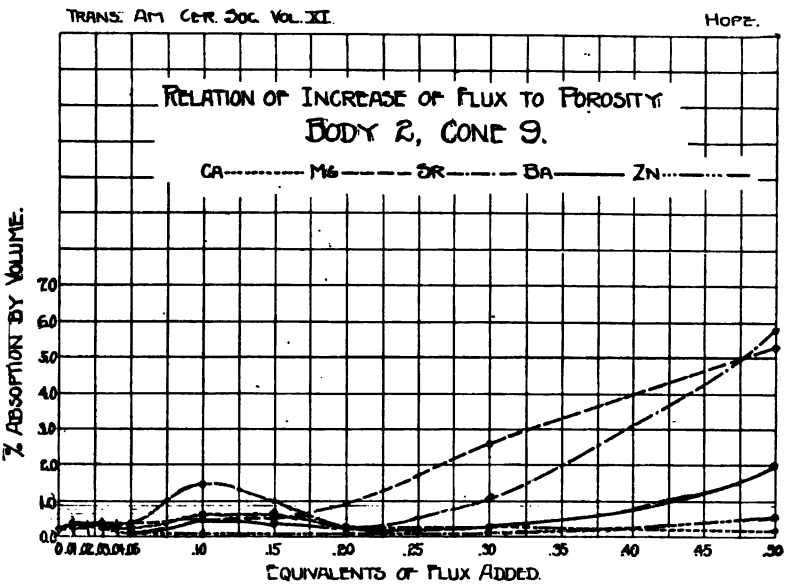
From these averages it will be seen that bodies 1 and 2 are of nearly equal strength and that both are considerably stronger than body 9, probably on account of the higher clay content of the latter. Mg is seen to give the best average strength, though as already noted, the best individual bodies are found in the Ca and Sr series of body 1.



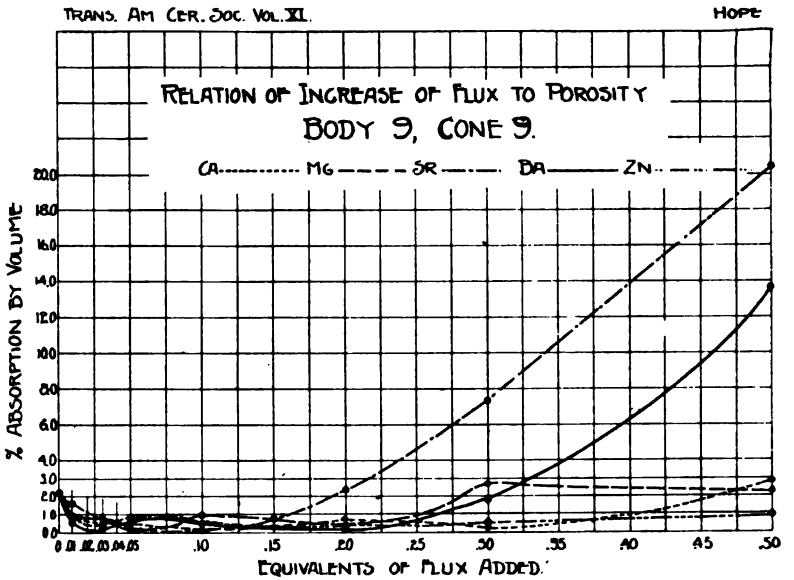
Absorption.

Ca shows a fairly regular curve for body 1, the closest mixture being that containing .1 eqv. In bodies 2 and 9 the curves are irregular, probably due to over-maturing of the body, most members of both these bodies showing under 1% absorption.

Mg shows a gradual but regular curve for body 1, the porosity varying very little after .05 eqv. In body 9 at the end of the series there is evidence of overfluxing, with consequent refractoriness, this quality being very marked in body 2 where the average porosity of "(h)" (.5 eqv.) is 10.9%.



Sr has a very regular and striking curve for body 1, the porosity increasing from 1.5% at .1 eqv. to 27.3% at .5 eqv. In body 9 the minimum occurs at from .05 eqv. (porosity 0.2%) to .1 eqv., while in body 2 the lowest porosity is at .01 eqv. (0.3%), rising rapidly at the end of the series to 10.2%.

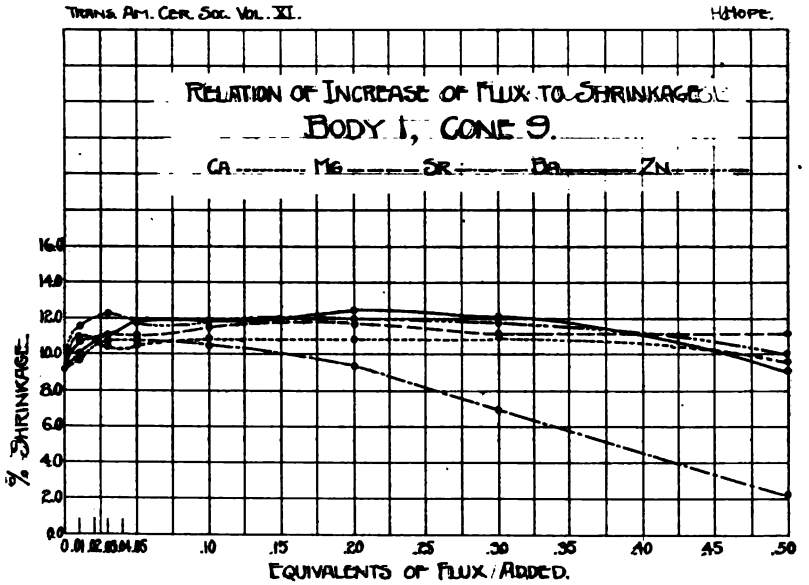


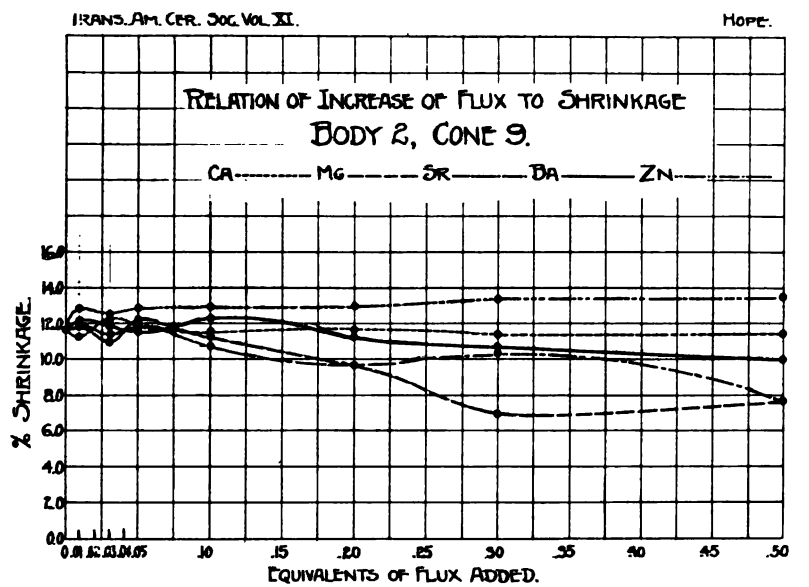
Ba shows a fairly regular curve for body 1, the minimum being at .1 eqv. to .2 eqv. addition. Body 9 gives with Ba perfect vitrification almost throughout the series, the porosity rising quickly towards the end of the series, an effect equally evident in body 1 and indicated in body 2.

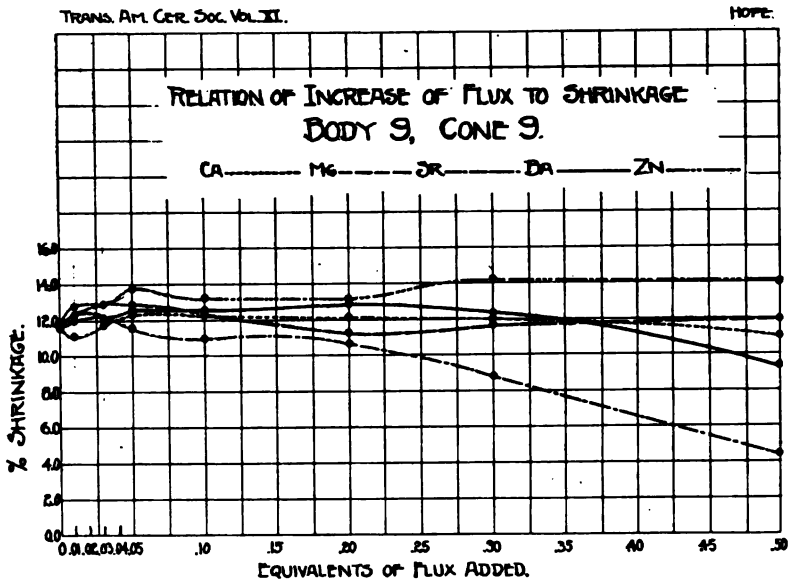
Zn has a somewhat irregular curve for body 1, the porosity rising rapidly at the end of the series; bodies 2 and 9 having more regular curves with minima at .2 eqv. in each case and also showing by the increased porosity at the end of the series that a refractory condition is being approached.

Shrinkage.

In general terms it may be stated that the shrinkage of these bodies is inversely as the porosity, and it will be found that the maximum shrinkage is either at, or very close to the minimum porosity, the minimum shrinkage being almost always at the end of the series where the overfluxed body again becomes refractory.


TRANS. AM. CER. SOC. VOL. XI.
HOPE.
RELATION OF INCREASE OF FLUX TO SHRINKAGE
BODY 1, CONE 9.
CA
MG
SR
BA
ZN
% SHRINKAGE.
EQUIVALENTS OF FLUX ADDED.


TRANS. AM. CER. SOC. VOL. XI.
HOPE.
RELATION OF INCREASE OF FLUX TO SHRINKAGE
BODY 2, CONE 9.
CA
MG
SR
BA
ZN
% SHRINKAGE.
EQUIVALENTS OF FLUX ADDED.



The only shrinkage curve worthy of particular note is that of Strontium which in body 1 falls to 2% at .5 eqv.

The shrinkage of the Barium bodies are high as a rule except at the end of the series, while those of the Zinc bodies containing 15 and 20% feldspar are excessive.

Color Comparisons.

Both Zn and Mg have a marked effect in improving the color of a body, the former having the greater effect, especially in very small quantities, .01 eqv. (about 1/6 of 1% by weight) being sufficient to distinctly whiten any of the three bodies used.

Sr is next in point of color and shows considerable improvement in bodies fired at cone 10, as do all the other fluxes in a greater or lesser degree.

Ba undoubtedly gives the worst color.

A comparison was made between cone 9 and 10 for relative color effects. The Ca series shows distinct improvement at Cone 10 at .01 eqv. and .03 eqv.

The Mg series shows very little improvement at Cone 10.

The Sr series shows considerable improvement at Cone 10 at .01 eqv. and .03 eqv.

The Ba series shows distinct improvement at cone 10 throughout series.

The Zn series shows marked improvement at cone 10 at .01 eqv. and .03 eqv.

Comparison for Blistering.

In the case of Ca, Sr and Zn, the pinholing or blistering is slight, being almost absent in the Sr bodies, while Mg and Ba exhibit this defect in a marked degree, the latter being somewhat the worst. The bodies showing the worst blistering are those containing .2 and .3 equivalents of flux, the body usually becoming more porous at .5 eqv. and consequently allowing the escape of the gas bubbles which the writer assumes to cause the blistering of the biscuit ware. The fact that $SrCO_3$ is extremely easy to decompose, and that $MgCO_3$ and $BaCo_3$ are very stable, may serve to explain the almost complete absence of blistering in the one case and of excessive blistering in the others, it being supposed that the CO_2 is completely driven off in the former before vitrification begins, and that in the latter, the gas is being continually disengaged, and, forcing its way through the softened mass of the body, leaves small holes which would, in the glost kiln, send up air bubbles through the glaze and cause pinholing. The blistering at cone 10 was almost identically the same as at cone 9.

GENERAL CONCLUSIONS.

CaO has no very striking characteristics as a flux as indicated in these experiments. It appears to produce some bodies of good strength, though rather poor in color, while the shrinkages are not excessive. Its tendency to blister seems to be slight.

MgO is shown by these experiments to be the most useful of the five fluxes studied. The excellent color of the magnesia bodies, together with their high average strength and moderate shrinkage, are evidence that they should be used more than hitherto; as the tendency to blister, while at high percentages of flux much greater than that of the other fluxes except barium, does not appear to be a serious factor if the proportion of flux is kept at or below .1 equivalent.

SrO has the advantage of giving a fairly white body at cone 9 which improves considerably at cone 10. It has the least tendency to blister of any of the fluxes used, and evidently gives some very tough bodies, such as 1—Sr d, with a Rattler loss as low as 0.5%. Its principal disadvantage is its present cost. The high porosity and low shrinkage obtained with high proportions of the flux are of interest.

BaO. This flux appears to have little to recommend its use; as the weakness of the Ba bodies, the very poor color it imparts, the somewhat excessive shrinkages and the blistering which is strongly in evidence where over .05 eqv. are used, may all be considered distinct disadvantages. It seems to impart better translucency than the other fluxes. A feature of the Ba bodies noticed in this work was their very sudden fusion, a slight increase of temperature changing the mass from a porous into an entirely vitrified condition.

ZnO. One of the chief advantages of this flux is the excellent color which it imparts to a body, even when in very small quantities, although above .05 eqv. it gives rather objectionable bluish or greenish tinge to the body.

Zinc bodies with 20% feldspar show a good average strength. This flux has the disadvantage of tending to opacify a body when over .02 or .03 eqv. are used; its bodies shiver badly with as low a content of ZnO as .1 eqv. in a body containing 50% flint, while in making the

trial pieces, the bodies containing a high percentage of this flux cracked badly on the moulds.

It will be observed from the shrinkage and porosity curves that the sequence of the most active fluxes is not the same for the three bodies. In body No. 1, with the highest silica content Ba increases shrinkage most decidedly, while in Nos. 2 and 9 Zn is most active. In regard to decrease in porosity Ba shows the lowest value in body No. 1, while in Nos. 2 and 9 it is difficult to differentiate the most potent flux since these bodies are already high in alkalies. In bodies No. 1 and 9 we also note distinctly the general fact that the first small additions of flux lowers the porosity most decidedly, the *rate* decreasing as the amount of base added increased. In body 2 this drop cannot be observed owing to the high initial feldspar content.

Other general conclusions cannot be drawn owing to the complexity of a ternary system with only three bodies employed.

The writer wishes to express his appreciation of the kind assistance of Prof. A. V. Bleininger and Mr. H. E. Ashley in drawing the conclusions presented herewith.

DISCUSSION.

Mr. Binns: Would it be possible, in the case of magnesia, to use the oxide, instead of the carbonate?

Mr. Hope: I would say we are trying that experiment at the present time. We have calcined a number of clays with magnesia and ground the magnesia, but found it set so hard that it was difficult to take it out. It may be a difficulty that can be overcome, but it was almost impossible to take it out.

Mr. Binns: Couldn't it be ground dry?

Mr. Hope: I think it would have to be.

Mr. Binns: I would like to know whether that shrinkage of magnesia, with which most of us are familiar, forms any bar to its use. I have always found that

magnesia produced such a high shrinkage in the body as to be objectionable.

Mr. Hope: I did not notice any excessive shrinkage with magnesia. It becomes very low where the porosity increases but where fifty per cent of feldspar is used it falls within the increase a little. Even then it is under eight per cent.

Notes by E. Mayer.

As I shall not have the pleasure of being present at the Rochester meeting of the A. C. S., I will make a few notes to be read when the discussion on Herford Hope's paper is in progress:

One of the first problems that confronts the manufacturer of vitrified china is to get a workable body—I mean a body that the potter can work without more loss than in the making of the average earthenware or W. G. body. In order to do this I persistently worked with English Ball Clays trying every brand I could get hold of and by that I mean some brands that have never been brought to this country for sale, but I failed to get a plastic enough body unless I used such a per cent that the color of the finished product was out of the question. I wish now to again pay tribute to that valuable paper by Mr. Ogden published in some of the early Transactions, because from that paper I got my first insight into the rational method of making vitrified china. Mr. Ogden in his experiments used one-half English Ball and one-half Tenn. Ball, and for his China Clay one-half English and one-half Florida. His finished product was not a passable color. The above mixture of clays is entirely impractical because 10% of English Ball, the very best you can get, even without the 10% of Tenn. Ball, is itself beyond the possibilities of making a salable piece of ware, on account of color. From my early training it was difficult to believe a body could be made without English Ball Clay, but I got a pointer from a friend who was using Tenn. Ball and a few trials

very soon determined the fact that Tenn. Ball Clay can be used in a China body to the extent of 15% and with a suitable China Clay will make ware of a beautiful color.

In making Vitrified China, toughness is one of the great features aimed at and this can only be gotten, as far as my experiments have gone, with the minimum amount of clay. This point cannot be too strongly insisted on. I have found in practice that the clay should be 40% of the whole mixture.

I also thought I had the minimum amount of feldspar when I used 15%, but from Mr. Hope's experiments which will be presented, I believe this is still excessive and that 12½% may prove to be a better per cent to increase toughness. In fact I have made some experimental bodies that looked well with 12½% spar, increasing the flint the 2½% taken off the spar and always keeping the clay at 40%. It must be carefully noted that all these remarks refer only to one temperature, cone 9, down flat, with 10 only slightly bent, if at all—the temperature I am now firing at.

As to the use of fluxes in a China body I am using lime and magnesia.

My experience with magnesia does not seem to agree at all with articles written on the subject in the *Transactions* and elsewhere. I never use it in excess of 0.4%, but it has a most marked effect on the color of the ware and is a wonderful aid to translucency. When I say 0.4% I mean that amount of Magnesite $MgCO_3$. Of lime I use 1.4% in the shape of Paris White ($CaCO_3$).

I have more or less trouble with blistering of the body and the cause of this is very difficult to detect. I have bothered many of my friends in England and the United States on the subject, but so far have received no very definite information.

I am now conducting some experiments with a view of lessening and I hope entirely stopping the trouble. My view of the matter is that the trouble comes from the

liberation of the CO_2 from whiting and magnesite. The CO_2 is said to come off only at high temperatures, especially from the magnesite and by calcining the magnesite and using bone as a source of lime this source of the trouble should be eliminated. Experimental work along this line seems to show that this theory is correct, but I have not made sufficient ware to prove it in actual working practice. The addition of bone not only does away with the CO_2 but in adding the phosphoric acid you get here another agent to help whiten the body, as it most unmistakably does. Three per cent bone is the highest amount I have used so far. Parmelee confirmed this theory of the action of phosphoric acid.

Referring again to blistering of the body I ought to state that this trouble exhibits itself in the form of pinholes in the glaze. These blisters on the surface of the biscuit ware are not visible to the *naked eye* and only develop as the glaze eats through the surface of the biscuit and forms a hole or crater which the glaze, if *thin,* won't bridge over and the result is a pinhole. The remedy is to put on a good thick coat of glaze and this entirely stops the pinhole from manifesting itself.

It may be objected to at once that a heavy coat of glaze may cause crazing. In practice I have never seen a piece of our vitrified china craze and don't think it is liable to on account of the heavy per cent of flint, 45%, and comparatively low content of spar, 15%. This body coupled with the fact that the glaze used has a high alumina equivalent content, viz., 0.4, reduces the liability of crazing down to a minimum.

In speaking of the blistering of the body, there are so many elements that enter into the question that I feel that we know, comparatively speaking, little on the subject and a vast amount of experimental work must be done before any definite result will be arrived at.

I desire particularly to call the attention of the Convention to the recent developments in Tennessee Ball

Clays—to some new discoveries that have been made, which give excellent results in both earthenware and china bodies. I shall be pleased to give any information I have to anyone desiring same.

Mr. Watts: I want to say a word myself in regard to the use of magnesium-oxide. I made some tests, published in an earlier record of the Society, with some plates. I distinctly remember using calcined magnesium oxide. I was making an oxi-chloride cement and had the oxide, so I used it. I was struck by the extreme whiteness of the porcelain—I think I made mention of it. Some time ago I was talking with Mr. Mayer on the subject of this peculiar pin-holing which he had noted, and his suspicion was at that time that it was due to magnesium—that it was blamable in some way to his carbonate. After I returned home I made a similar porcelain in which I used different spar and a different flint, but using calcined magnesium oxide. I could not see in my trials with a strong handglass, any evidences of these little holes which I could readily see in those he showed to me at New Brighton. I think from my viewpoint, there is no doubt but that magnesium oxide would materially reduce if not overcome the difficulty.

Mr. Stover: I had a little problem myself. A friend of mine, making spark plugs for automobiles, had a difficulty in regard to their splitting. They would get red hot and stop the machine and when at a red heat they would shatter off. He wanted to get a spark plug that would cool down from a red heat in a cold draft. I recommended magnesium as a good flux. I think the experiment that was the most successful was one with half magnesium sulphate and half magnesium carbonate. In some of my own experiments, before turning them over to my friend, I found that about one-half of the mixture made a very tough body; that I could bring it to a red heat and put it into a cold bath without its splintering. I couldn't get that with a lime flux.

One to two per cent of the total body mixture was sufficient.

NOTES ON THE USE OF CHROMATE OF LEADS AS AN INDICATOR FOR ACID AND BASIC FLUXES.

BY

WILLARD L. BRUNER, Perth Amboy, N. J.

Since many problems in ceramics depend on the use of so-called acid and basic fluxes, it seems to the writer that it would be quite scientific to have some means of determining the state of acidity or basicity for any individual flux, rather than be obliged to compare two fluxes and call the one more acid than the other because its acid contents are higher.

The simplest means of accomplishing this is by the use of some chemical which is capable of acting as an indicator. Chromate of lead is suitable for this purpose. Analytical chemists base their acidimetric work on the use of various indicators in which the free acid or free base has a definite color or is colorless, and the corresponding salt has a different color. The theory upon which the use of Lead Chromate is based is simply this: There are two chromates of lead, the one is basic ($PbO\ Cro_3\ PbO$) and red in color, the other is normal or neutral ($PbO\ CrO_3$) and yellow. Using chromate of lead in a basic flux, the basic compound is formed and the resulting fritt is coral red colored and opaque, showing that the basic chromate is insoluble in the flux; by using chromate of lead in an acid flux the normal chromate is formed (there being no acid chromate of lead), and the resulting fritt is silver yellow and transparent. These two colors are clearly defined and are not obscured by intermediary tones, the chief requisite for success being not to overfire. It is unessential whether the red or yellow chromate

of lead is used, the resulting color will be red if the flux is basic and yellow if acid.

Up to this point the problem is simple enough. The real difficulty begins when we face actual conditions in practice. In the first place this reaction is only of value when applied to low-melting fluxes, such as are used for glass colors or soft over-glaze colors. The accuracy of the test is far from what is scientifically desirable, due partly to the increasing solvent power of a flux for red chromate of lead with the rising temperature, but more particularly to the large amount of indicator (20—30%) necessary to obtain results.

THE COLLOID MATTER OF CLAY AND ITS MEASUREMENT.*

HARRISON E. ASHLEY, Pittsburg, Pa.

In this paper a definition of clay is given sufficiently broad to include all substances worked as clays. The colloid theory is then applied to a description of the properties of clays. The endeavor has been made to use, so far as possible, only studies on clays, avoiding studies on other colloids, such as gelatine, albumens, metallic sulphide suspensions and metal suspensions. Special attention is given to adsorption, that property, so well developed in colloids, of taking other substances out of solution or suspension. It is finally shown that the adsorption of certain dyes by clays furnishes a means of estimating the colloidal matter present, and that when classified according to colloidal contents the clays are also classified approximately according to plasticity. This latter investigation was commenced while the writer was in the employ of the Homer-Laughlin China Co., Newell, W. Va., and is being continued in the Clay Products Laboratories of the United States Geological Survey.

DEFINITIONS.

A colloid may be defined as anything that is not crystalline; so that matter may be described as either crystalline or colloid. The highly developed organic structures go in the crystalline group.

Clay is a mixture of crystalline minerals of which the representative members are silicates of aluminum, iron, the alkalies, and the alkaline earths. The hydrated aluminum silicate, kaolin, (Al_2O_3 . 2 Si O_2 . 2 H_2 O)

*By permission of the Director of the United States Geological Survey.

is the most characteristic of these. Some feldspar is usually present. The grains of these minerals may show crystal faces, but more commonly they are of irregular shapes. Upon most of these grains is an enveloping colloid coating. This is mainly of silicate constitution, but may consist partly of organic colloids, iron, manganese, and aluminum hydroxides, and of hydrated silicic acid. Quartz grains, which are generally present, and mica, which is frequently present, do not have the colloid coating, or have it in much less degree than other grains. Almost any mineral may be present in clay and modify the properties somewhat. The combination of granular materials and colloids is in such proportion that, when reduced to sufficiently fine size (by crushing, sieving, washing, or other means) and properly moistened with an appropriate amount of water, plasticity is developed. Most clays exhibit the colloidal form to the eye, the crystal grains being largely concealed by the colloid coating.

ISOLATION OF COLLOIDS.

In 1874 Th. Schloesing (1) allowed a sample of 40 grams kaolin to settle for 27 days. 0.59 g. remained in suspension. This was precipitated by an electrolyte, filtered, washed, put into a porcelain dish, and dried over calcium chloride. It became a broken film, horny, slightly translucent, adhering strongly to the porcelain. The sediments had almost no cohesion, the coagulated suspension (e) a great amount. There was no gradual change from the last sediment to the horny matter, but an abrupt difference in properties. Schloesing concluded, "From these characteristics, I consider that the clay e is colloidal."

FORMS OF COLLOIDS.

Colloids exist in two characteristic forms: (1) the homogeneous suspension in a liquid, called "sol"; and (2) the continuous jelly with pore walls (and pores) filled

with a liquid, called "gel". Solids are included under (2) as a limiting case. The sol or gel is named by a prefix according to the liquid with which it is associated: as hydrosol, alcosol, hydrogel, etc. This nomenclature proposed by Graham (2) in 1861 has been generally adopted, and is preferable to the terms "colloid" for sol only and "pectoid" for gel, recently used by Cushman.

Colloids are commonly spoken of as reversible and irreversible, according to whether they will pass from sol to gel, and back to sol; or whether, having passed into the gel form, they cannot be re-converted to the sol. The process of passing from sol to gel is best called "coagulation", though sometimes "pectinization" is used. The reverse process is called "deflocculation" or less advisedly "peptinization".

Charcoal is an example of a gel that has been "set" permanently by heat, there resulting a very complete decomposition of the organic gels present, and the final structure depending on their structure. Liquids are not *absorbed* into the substance of its pore walls, but dissolved substances (solutes), or suspended substances (sols), are readily attached to the surfaces of its pore walls (adsorption). All of the external and internal surfaces are wetted by the liquid.

NATURE OF COLLOID SUSPENSIONS OR SOLS.

Quoting Whitney and Ober (3):

"A clearer idea of the value of what follows will be gained if one recognizes at this point the probable necessity of attributing electrostatic charges to particles of any kind when suspended in a liquid, and of assuming that these charges, while they may be positive or negative for different kinds of suspended matter, must still be of the same sign for all particles of the same substance. It is known that two different substances in contact assume equal and opposite electrostatic charges at their contact surfaces, and the work of Quincke, Coehn, and others have brought to light the regularities of this phenomenon.

"Suspended particles of finely divided sulphur, silica, (probably also non-gelatinous clay) etc., in water, exhibit negative charges exactly as larger masses of the same substance in contact with water do, and when the suspension is placed between two electrodes connected with a source of electromotive force, the particles all migrate in the direction of the negative current. . . .

"Spring (4) believes the statical charge, which it is assumed the ions of electrolytes carry, neutralizes the statical charges of opposite sign on colloidal particles. . . . For example, he states that certain colloids are negative, and therefore require for their immediate precipitation or coagulation a certain concentration of a positive ion".

. . . the hydrosol condition is bound up with the presence of certain ions in the colloid, which are added naturally to the colloid as electrolyte or remain in the same". Dialysis decreases stability and leads to precipitation. Increase of the same electrolyte increases stability up to a maximum, then lets it fall to zero.

SETTLING OF CLAY SUSPENSIONS.

J. M. Van Bemmelen (5) went into the question of the settling of a clay suspension. As soon as the loosely bound salts are washed out of a clay it becomes difficult to cause it to settle, and it cannot be filtered, but runs thru the filter paper. On adding a small amount of acid or a salt or an alkali (in short, any electrolyte) the milk-white liquid coagulates and settles in a short time. It also can now be filtered. Washing again with water, another point is reached when the particles become infinitely fine and pass thru the filter.

Experiment.

The writer has verified this experiment (making sketch on board): He took a mixing jar of one litre capacity and placed in it one litre of water, and into that about 100 grams of No. 1 N. J. Sagger clay. Then it was shaken about a minute and allowed to stand about half an hour. At that time it had settled perfectly clear to about 100cc (indicating). The clear water was siphoned off, the jar refilled, shaken, and allowed it to settle another half hour. These operations were repeated eight times.

The first decantation was very clear; the second was turbid, and the others so turbid that one could not see light thru them in the jar.

To estimate the amount of water that would allow the passage of light, this apparatus was used—a graduated flat bottom glass cylinder with a cock near tne base (indicating)—to measure the turbidity. Filling this cylinder with the clay, a newspaper print was placed underneath it, and drawing off the water the graduation on the tube was read when it became so shallow that the print could be read. The fifth of the successive decantations of one litre each showed maximum turbidity. The material contained in this bottle (exhibiting same) was taken from the fifth decantation.

There was another peculiarity noticed. In the case of the first decantation, after standing 24 hours, there was no sediment in the bottom of the clear liquid; in the case of the next two, slight sediment. In the others, there was about a quarter of an inch of sediment in each case. It is believed that not only the colloidal matter, but even the finest granular matter had electric charges sufficient to enable it to stay up in suspension for a considerable time when the precipitating salts had been removed by the pure water.

Van Bemmelen assumes that the finely divided substance forms large molecular aggregates in which the added substance takes part. The solution to do this must have a definite concentration; otherwise, too many molecular aggregates are decomposed by the water and return to the finer molecular condition.

NATURE OF GELS.

Some of the simpler colloids, such as those of the nobler metals, probably do not form gels at all; their decomposition is always the irreversible one to set gels. Those substances that form gels are apparently such as have a tendency to form crystals, and especially complex and hydrated compounds under favorable conditions. With the reaction of gel-formation, sufficient freedom is not apparently given the particles to orient themselves into crystal ranks. The precipitation seems to take place when the particles get within a certain maximum range of each other. This probably gives a certain regularity of structure which microscopic workers describe as cellular. The precipitating ion, when the cause is the action of an electrolyte, also tends by its presence to break up the symmetry of arrangement required for crystals. The precipitate is then a confused mass, with positive and neg-

ative valences satisfying each other where near enough, but possibly with many unsatisfied valencies about. The more complex the chemical ion and the more viscous the medium, the more unlikely it is when concentrated by itself or precipitated with a substance of opposite electrical sign that the complex ions of a substance will ever be able to arrange themselves on crystal lines. Heat, giving greater mobility, tends to assist those complex sols to arrange themselves in such a manner as to precipitate or coagulate; while the simpler ones, having at all times sufficient mobility, require merely the oppositely charged electrolyte. Heat may also assist by decompositions to simpler molecules and by the increase of static charges. This leads to the conception of permanent colloids which, in short, are substances that never find conditions favorable for coagulation. Such probably have only small electrostatic charges in proportion to their mass; so that but little effect upon their properties results from the neutralization of that charge by an oppositely charged ion. Even the formation of gels may not be noticeable in some such cases.

When a very stable sol in the presence of a less stable sol of the same sign is acted upon by an electrolyte that will not precipitate the former, but would precipitate the latter if alone, the influence of the more stable sol is often sufficient to "protect" the less stable sol from coagulation. Non-colloidal substances can exercise protection, e. g., ether protects noble metal hydrosols. Thus gelatine is a common "protection colloid" for many substances of small-sized ions. The colloids of clay may carry mechanically into suspension solid particles that are wholly non-colloidal by ordinary ideas.

PLASTIC BODIES

Many plastic bodies consist of a more or less granular material, coated and held by a viscous substance; e. g., putty, a mixture of any white granular material (typically

whiting) with linseed or a similar oil, the latter hardening on exposure to air; cake frosting, a mixture of granular sugar with the white of eggs, becoming hard on exposure to air; plaster paris, a mixture of gypsum crystals and an amorphous paste of uncrystallized plaster, hardening upon completion of the crystallization; wiping solder, a mixture of lead crystals, in a fused eutectic mixture of lead and tin, hardening on cooling; mortars, mixtures of sand with lime or other cementing pastes, hardening on reaction with the air, or by internal reactions; waxes, mixtures of oils of high melting points with oils of lower melting points, hardening on cooling; and finally clays, mixtures of granular, non-plastic materials with moist organic and inorganic gels, hardening on evaporation of the water.

HYDROXYL THEORY OF PLASTICITY

P. Rohland (6) considers that the plasticity of clays depends upon the amount of hydroxyl ions (negative) present in the water. When this is large, the negatively charged clay particles will go into suspension. When the hydroxyl concentration is depressed, as by additions of acid, or depression of temperature, the clay will assume the gel condition and become plastic.

Experiment.

Showing the different effect of sol and gel states of a clay upon its fluidity.

In a shallow dish is put 130cc. water, and 150 grams J. Poole's No. 1 English China Clay is stirred in. This makes a thick paste, and, with care the dish may be turned bottom side up without the contents falling. Now stir in 2.4cc. of 2.5 normal sodium hydroxide. Enough of the gel is converted to the sol state so that the thin slip formed may be poured back and forth into another vessel. If the sodium hydroxide is neutralized by 2.4cc. of 2.5 normal hydrochloric acid, the mass again stiffens by gel formation, so that the dish can again be held bottom side up without loss.

PLASTICITY DUE TO FORMATION OF MOST STABLE GEL BY REACTION OF A POLYVALENT ION OR A COMPLEX GROUP

According to Hardy (7), a sol is coagulated when its static charge of electricity is neutralized. This is usually by electrolytes. With a negative sol, such as clay that has been brought into colloidal suspension, the positive ion of the electrolyte is of most influence in effecting

precipitation, the acid ion taking little part. The power seems to vary but little in different positive ions of the same valence; but divalent ions have many times the precipitating effect of monovalent ions, and trivalent ions still more (31, 3, 32).

Let us consider the action of sodium carbonate on a clay which we will assume has just enough calcium (the most common "soluble salt" in clay is calcium sulphate) to keep the colloid matter in gel form. As the calcium is but loosely combined, it will react according to the following equation:

$$\underset{\text{with gel}}{Ca} + \underset{\text{the addition}}{Na_2CO_3} = \underset{\text{insoluble}}{CaCO_3} + \underset{\text{with the sol}}{Na_2}$$

This relation was first perceived by F. Förster (33).

The calcium carbonate formed, being insoluble, no longer has influence on the colloid. The sodium, in amount equivalent to the calcium, has metal ions of lower valence than the calcium which originally stabilized the gel. As many times more sodium atoms than calcium atoms are required to coagulate the same amount of gel, it is evident that the clay gel will be broken up, or deflocculated by the soda, and the plasticity will fall off in proportion to the completeness of the reaction. When, however, enough sodium ions have been added, we may expect them to coagulate the gel anew. Such is the case, as studied by Mellor, Green and Baugh (8). These investigators took measurements of the time required for 200 cc. of an earthenware body slip to run from a modification of Mariotte's bottle. Reduced to a basis of time for water equals ten seconds, their results were:

Add. in grams.	0	0.1	.2	.3	.4	.5	1.0	1.5	2.5	3.5	4.5
Time in sec...	10	8.7	7.4	6.5	6.1	6.1	6.1	6.1	7.8	13.9	*

When the added salt does not form an insoluble product with the salt in the clay, there is probably partial replacement in accordance with the mass action law. Thus

*The asterisk denotes that the slip was too stiff to flow through the apparatus.

on addition of sodium sulphate, there was a falling off in viscosity, and sufficient sodium ion concentrations were not reached to coagulate again the gel. Certain salts, however, were added in sufficient amounts to coagulate the gels again. Divalent ions in some cases reinforced the salt in the clay; in others the reverse, according to slight variations in coagulating power. Trivalent ions reinforced the flocculation, even though associated with monovalent ions.

The effect of the complexity of the NH_4 group may be of influence similar to high valence, or it may have a solvent effect on set organic gels, in either case increasing viscosity. Alcohol substitutions for water increased the viscosity. The action of alcohol is therefore similar to that of ammonia, a complex group, with solvent effect on organic matter.

Humic acid and grape sugar, being themselves colloids, increased the colloid content and the viscosity.

Inorganic sols (10) are frequently coagulated by freezing or evaporating, and this is often really due to the trace of electrolytes always present in the liquid, which becomes concentrated in the remaining liquid till it reaches the minimum necessary for flocculation.

Experiment on Viscosity of Clay Slips.

Bleininger has made an investigation of the viscosity of clay slips with different percentages of clay and water. He found with the three clays tested that the most plastic had the greatest viscosity. The operation of apparatus similar to Mellor, Breen and Baugh's will be illustrated. The first experiment is made with a sample of Tennessee Ball Clay No. 3 obtained from the Potters' Supply Co. (Exhibiting sample.) It was ground about an hour in a ball mill, sifted thru a 120 mesh lawn and has been standing about 48 hours. The time it takes for 200cc. slip to flow from the opening in the bottom will be measured (placing brass cylinder containing slip over glass graduate cylinder, which latter was set in front of an electric light). It has taken one minute and twenty-nine seconds. (Removes cylinder and washes same, returning it to position on the table). Here is also a sample of No. 1 English China Clay, obtained from Mr. Joshua Poole. (Timing same.) In this case it has taken one minute and twenty seconds; or, it took the ball clay nine seconds longer than it took this china clay. In this case Mr. Bleininger's results have been verified, tho it would require comparisons on quite a number of clays to know how general the principle is.—to what extent it will hold, that viscosity shows the plasticity of the clay.

MEASUREMENT OF COAGULATING POWER

According to Hardy (7), in the case of the action of salts on hydrosols, equicoagulate solutions agree in their electric conductivity when the valence of the active ion is the same, but the mathematical expression contains a factor which is approximately squared or cubed by a change from a monovalent to a di- or tri-valent ion. The relation can therefore be best expressed as $K = nx(u+v)\ A^x$, where K=specific conductivity; x is the fraction of the total number of molecules n which are dissociated at any one moment; (u+v) is the sum of the velocities of the two ions; A is a constant where x is positive and increases rapidly with an increase in the valency of the ion whose electric charge is of the opposite sign to that of the particles.

ABSORPTION OF MOISTURE.

According to Bemmelen (12), hydrogels are not definite hydrates; as the vapor tension and hence the water content changes continuously with temperature, while a true hydrate gives off a definite number of molecules of water at definite temperatures. The water of hydrogels may be replaced by other liquids, such as alcohol, glycerine, etc. The aqueous tension of colloids also undergoes irreversible changes on drying out, heating, etc.

The large moisture content of air dried clays is not to any noticeable degree due to the feldspar and quartz, but to the organic matter and to the mineral colloidal constituent of the clay.

It has been pointed out by Weber (13) that the water associated with a gel is *dissolved in the gel*—a distinction from ordinary solutions with a considerable difference. Van Bemmelen (14), states that it is homogeneously distributed throughout the substance of the gel, not concentrated on the surfaces like hygroscopic water on glass.

WEATHERING AND AGEING

The development of plasticity by weathering, in the case of fire clays, consists of a re-absorption of water that

was originally present in the clay, but has been removed by ages of pressure in its place of deposit. It is similar to the soaking up of water by a sponge.

With a body containing feldspathic matter ageing is of a different nature. It must continue until, first, the decomposition of feldspar by water into colloidal silicates, colloidal silicic acid (?) and free alkali (15) has ceased or become greatly retarded; and until, second, this free alkali has been neutralized either by acids originally present in the clay, or more likely by the products of bacterial activity (16) in the ageing clay.

NO DIVIDING LINE BETWEEN COLLOIDS AND CRYSTALLOIDS.

A colloid of opposite sign may perform the same function as a salt ion of opposite sign in coagulating a sol or stabilizing a gel. According to Teague and Buxton (17, 18), (whose work does not seem to be published in the language of their own country) some dyes are true crystalloids, soluble in water; others, true colloids, suspensions in water; and there are all intermediate gradations. In other words, there is no dividing line between crystalloids and colloids; but it is convenient to classify separately as colloids those substances whose ions are so large as to give pre-eminence to those phenomena that we call colloidal. But all dyes can be treated as in one group.

Mixtures of two colloids of opposite signs cause a precipitation which is complete at a definite proportion, but addition of an electrolyte capable of precipitating one of the two colloids prevents their mutual precipitation.

ADSORPTION.

After a sol has been precipitated, carrying down a certain amount of an opposite ion, the question is proper, What becomes of the excess of the precipitating ion? or of other ions of the same sign that may subsequently be brought into the liquid? The replacements possible in the latter case have already been discussed. There are two views: The one, that the excess ions are collected on the

surface of the gel, adsorbed, as is considered the case with gases held by charcoal; the other, that the excess ions are distributed between the outside liquid and the gel, as if the gel were the second of two immiscible liquids, i. e., that the ions were held in solid solution in the gel.

Walker and Appleyard (19) have disproved the latter theory as applied to dyeing, and their proof is equally applicable in other cases. The adsorption theory, not having been disproved, probably is correct. For this theory, it is necessary to consider that the gel has a surface proportional to its mass. The circumstances that may lead to a cellular structure have been mentioned. W. B. Hardy (7) discusses such a state in the case of gelatine. Van Bemmelen (20) notes the similarity of such structures and emulsions. Lottermoser (21) describes a cell-like structure, which he calls an "emulsion colloid", but which Weber (13) has described as a gel swelled up to, near, or above the maximum solubility of water in the gel. Butschli and also Nagelli have described the microscopic appearance of the cellular structure of colloids.

The mathematical study of adsorption did not lead to any conclusive results in the present investigation.

MEASUREMENT OF PLASTICITY.

Assuming that the plasticity of clays is mainly due to a proper ratio of granular materials and colloid gels, it seemed that any means of establishing the relative or absolute amount of colloids in a clay should supply a measure of its plasticity.

Hirsch (22) in his account of "The Behavior of Clay in Salt Solutions", saw the possibilities of adsorption. He said, "We hoped at first to be able to classify the clays according to their plasticities with the help of this process (adsorption of barium chloride). The lean, very sandy brick clays fall completely out of the series, and partially show a greater adsorption than the fat, highly

plastic clays". Having somehow acquired the information that colloids adsorb dyes, but without any details, I also sought to apply this principle to the measurement of plasticity.

The dye so far giving best results is malachite green.

The following procedure was adopted: Into a 500 c. c. bottle with ground glass stopper, greased with vaseline, 20 grams clay and the dye were placed, then 400 c. c. water was added. The closed bottle was then fastened in the frame of a small ball mill (60 rev. per min.) so that at every revolution it was upended. This gave a vigorous and complete agitation, which lasted for an hour; the results were too large and erratic unless the settling continued over night. On the following day a convenient amount of the clear liquid was taken out by a pipette and put into one of a pair of "carbon" comparison tubes such as used in steel analysis, and compared by dilution with a standard solution of three grams per liter, using a camera while matching.

ADSORPTION OF MALACHITE GREEN AND OTHER PHYSICAL PROPERTIES.

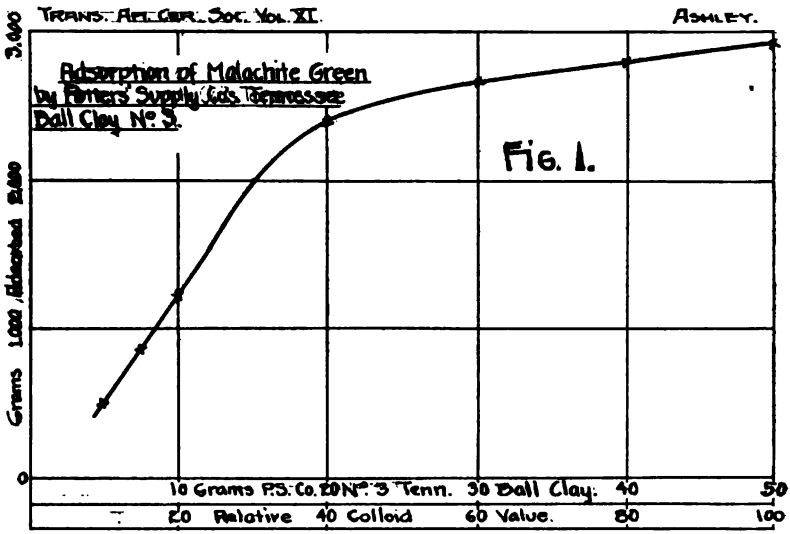
	Portion Unadsorbed		A	B		C	D	E	F	G
	1.00 gms. dye used.	3.00 gms. dye used.	Jackson-Purdy Surface Factor	Cast Air Shrinkage	Fire Shrinkage Cone 8	Relative Colloids	Surface Concentration of Colloids $\frac{C}{A} = D.$	Specific Air Shrinkage of Colloids $\frac{B}{C} = E.$	Deformability $D \times E = \frac{B}{A} = F.$	Plasticity $C \times F = \frac{C \times B}{A} = G$
Fullers' Earth, Eimer & Amend	.00081	.00351	121	25.0	23.0	.....	.....	.....	.2066	.....
"Lone Star" Texas "Kaolin" (5 g., 0.0456; 7.0 g., 1.291)	perfectly clear	.01075	123	12.0	12.8	154.0	1.250	.0780	.0977	10.34
A. H. Williams Texas "Kaolin"	.....	.01994	.....	18.6	13.2	139.0	.....	.1336	.....	.....
Potters' Sup. Co. Tenn. No. 3 Ball	.....	.03608	184	8.5	10.5	100.0	.544	.0850	.0462	4.62
Jas. P. Prall, No. 1 Lt. Sagger	.....	.04700	168	12.2	8.9	100.0	.597	.1220	.0727	7.27
J. Poole, Pike's No. 20 Eng. Ball (2.0 g., 0.0276; 4.0 g., 0.2855)	.00371	.06990	185	11.9	11.6	97.5	.527	.1220	.0643	6.28
Pfister & Wüstl, Lischwitz, Bohemia	.....	.06800	.....	8.5	10.8	97.5	.....	.0872	.....	.....
G. Knowles & Sons No. 12 Eng. Ball (2 g., 0.0270; 4 g., 0.2855)	.00860	.07640	170	11.5	9.7	96.5	.568	.1191	.0677	6.53
Mandle-Sant Clay Co., Tenn. No. 3 Ball	.00333	.08480	184	11.5	11.0	95.2	.517	.1207	.0626	5.96
Hammill & Gillespie, Whiteway's Eng. Ball	.....	.10900	.....	9.8	13.0	92.0	.....	.1064	.....	.....
Moore & Munger, Eng. Ball	.00258	.11210	199	10.7	7.1	90.7	.455	.1181	.0538	4.88
Kentucky Cons. & Imp. Co., No. 1 Sagger	.....	.18600	173 (dyed)	11.3	8.6	87.0	.502	.130	.0654	5.69
Mandle-Sant Clay Co., Special Sagger	.00445	.15910	113	12.0	5.9	85.5	.757	.1404	.1062	9.09
Johnson-Porter Clay Co., No. 9 Tenn. Ball	.01635	.19550	170	12.3	10.2	79.7	.468	.1544	.0724	5.76
P. L. Ryan, No. 1 Sagger	.00477	.20830	150	9.2	5.5	78.0	.519	.1176	.0613	4.79
Atlanta Mining & Clay Co., (Washed China Clay)	.....	.21900	152	9.4	7.6	76.7	.504	.1224	.0618	4.73
G. Knowles & Sons, No. 4 Eng. Ball	.....	.23500	.....	7.5	11.3	74.9	.....	.1000	.....	.....
Excelsior Ball Clay Co., Sagger	.00731	.22880	172	9.7	7.9	74.5	.433	.1301	.0564	4.20

ADSORPTION OF MALACHITE GREEN AND OTHER PHYSICAL PROPERTIES.

	Portion Unadsorbed		A	B		C	D	E	F	G
	1.00 gms. dye used.	8.00 gms. dye used.	Jackson-Purdy Surface Factor	Cast Air Shrinkage	Fire Shrinkage Cone 8	Relative Colloids	Surface Concentration of Colloids $\frac{C}{A}=D.$	Specific Air Shrinkage of Colloids $\frac{B}{C}=E.$	Deformability $D\times E=\frac{B}{A}=F.$	Plasticity $C\times F=\frac{C\times B}{A}=G$
Potters' Sup. Co., Tenn. No. 4	.....	.25500	179	11.3	11.7	71.3	.399	.1585	.0633	4.52
Edgar Bros. Co., No. 8 Sagger	.00268	.26300	178	9.0	9.0	69.5	.390	.1293	.0505	3.51
Johnson-Porter Clay Co., No. 10 Tenn. Ball	.02060	.27920	183	10.0	9.8	67.5	.369	.1482	.0512	3.45
Mandle-Sant Clay Co., Tenn. No. 11 Ball	.....	.28600	.....	9.4	10.5	66.8	.....	.1405	.....	.....
William H. Prall, No. 1 Retort	.....	.28280	117	8.6	6.9	66.7	.570	.1289	.0735	4.90
Mandle-Sant Clay Co., A-1 Tenn. Ball	.....	.295	.....	12.0	9.0	66.0	.....	.1818	.....	.....
J. R. Such, B B Mixture (Sagger)	.02235	.316	168 (dyed)	9.7 Total	9.3	63.5	.3780	.1527	.0577	3.660
Wm. H. Cutter, Sagger	.....	.372	129	15.0	.....	56.5	.4370	.....	.....	.....
Edgar Bros. Co., No. 10 Sagger	.00872	.494	137	8.0	5.0	45.0	.3280	.1775	.0583	2.633
Paul Clay Co., Ground Sagger (fireclay)	.02325	.578	78	5.0	2.0	40.5	.5190	.1234	.0641	2.595
Mandle-Sant Clay Co., Georgia China No. 1	.....	.683	.....	.....	.....	37.4	.....	.....	.....	.....
Johnson-Porter Clay Co., U. X. Sagger	.....	.775	187	9.6	8.8	35.5	.1898	.2700	.0513	1.824
Edgar Plastic Kaolin Co., Florida Clay	.03430	.925	(dyed) 85	14.8	9.0	32.5	.3820	.4550	.1740	5.660
Wilholm Priem, Zettlitz (Germany) Kaolin	.....	.938	191	7.9	6.3	32.3	.1692	.2440	.0413	1.335
W. J. Allen, "Hill Clay" (surface fire clay)	.....	.967	.....	.....	.....	31.8	.....	.....	.....	.....
Diamond Clay Co., ground fire clay	.01895	1.058	59	.....	2.0	30.4	.5160	.0000	.0000	.0000
Mandle-Sant Clay Co., Tenn. No. 9 Ball	.02300	1.137	192	9.7	9.2	29.2	.1542	.3320	.0504	1.473
Wm. Adolph Co., WH. Eng. China Clay	.04610	1.146	199	7.6	7.7	29.0	.1456	.2615	.0381	1.104
Harris Clay Co., Bryson China Clay	.02990	1.152	163	6.2	5.5	28.9	.1773	.2144	.0380	1.097
Johnson-Porter Clay Co., No. 1 Ball	.....	1.187	188	9.2	7.8	28.2	.1499	.3260	.0488	1.378
Hall Clay Co., Georgia Sagger (Kaolin)	.07590	1.230	178	8.6	8.0	27.7	.1555	.3105	.0482	1.335

ADSORPTION OF MALACHITE GREEN AND OTHER PHYSICAL PROPERTIES.

	Portion Unadsorbed		A	B		C	D	E	F	G
	1.00 gms. dye used.	3.00 gms. dye used.	Jackson-Purdy Surface Factor	Cast Air Shrinkage	Fire Shrinkage Cone 8	Relative Colloids	Surface Concentration of Colloids $\frac{C}{A}=D.$	Specific Air Shrinkage of Colloids $\frac{B}{C}=E.$	Deformability $D\times E=\frac{B}{A}=F.$	Plasticity $C\times F=\frac{C\times B}{A}=G$
Harris Clay Co., Bryson China Clay	.02990	1.152	143	6.2	5.4	25.8	.1804	.2400	.0433	1.117
Potters' Sup. Co., Wad Clay	.03100	1.357	133	9.2	4.3	26.7	.1932	.3580	.0692	1.775
J. Poole, B B Eng. China Clay	.....	1.440	198	7.0	1.2	24.7	.1246	.2830	.0353	.873
Golding Sons Co., Glaze Feldspar	.....	1.456	.....	.....	Melts	24.5	.....	.....	.....	.....
Hammill & Gillespie, A-1 Eng. China Clay	.08420	1.459	175	6.2	6.4	24.5	.1397	.2526	.0354	.868
J. Poole, No. 1 Eng. China Clay	.04080	1.500	175	8.1	5.6	23.8	.1358	.3398	.0462	1.097
Moore & Munger H. N. Eng. China Clay	.0523	1.554	186	5.4	7.3	23.1	.1241	.2332	.0292	.675
Mandle-Sant Clay Co., Monroe Wad Clay	.0892	1.606	134 (dyed)	9.2	1.8	22.3	.1665	.4120	.0686	1.530
Johnson-Porter Clay Co., X Wad Clay	.0935	1.616	101 (dyed)	9.0	7.0	22.2	.2195	.4040	.0841	1.867
Peter S. Duncan, White Mountain (Pa.)	.....	1.808	144	6.6	13.0	19.7	.1366	.3350	.0458	.903
John Sant & Son, Bluemont China Clay	.....	1.860	156	7.6	6.2	18.8	.1204	.4035	.0487	.916
J. Poole, I. R. & S. Eng. China Clay	.....	1.883	.....	9.0	7.8	18.6	.....	.4830	.....	.....
Peach Kaolin Co., China Clay	.0692	1.886	170	5.1	4.8	18.5	.1086	.2754	.0300	.556
Moore & Munger, M. C. R. Eng. China Clay	.0758	1.929	178	6.4	6.9	18.0	.1007	.3550	.0359	.647
G. Knowles & Son, No. 15 Eng. China Clay	.1042	2.060	163	6.3	7.1	16.0	.0982	.3930	.0386	.618
G. Knowles & Son, No. 7 Eng. China Clay	.....	2.410	.....	7.0	5.9	11.5	.....	.6080	.....	.....
Maine Feldspar Co., Feldspar	.2990	2.528	122	.....	Melts	.....	.....	.....	.....	.....
Eureka Flint & Spar Co., Conn. Glaze Feldspar	.....	2.558	.....	.....	Melts	9.4	.....	.....	.....	.....
Trenton Flint & Spar Co., Maine Feldspar	.....	2.760	.....	.....	Melts	5.7	.....	.....	.....	.....
Potters' Mining & Milling Co., "Flint" quartz	1.000	3.000	126	.....	.....	.....	.....	.....	.....	.....



DISCUSSION OF TABULATED RESULTS.

The results with 3.00 gram dye per 50.0 grams clay in 1000 c. c. water are used as a basis for comparison. From these, column C has been prepared by means of Fig. 1. The principle is this: if there is a certain amount of colloids in, say, 10 grams of No. 3 Ball Clay, there is twice as much in 20 grams, three times as much in 30 grams, etc. Let us call the amount of colloids in 50 grams 100, in 20 grams 40, etc. Treating each of these amounts of No. 3 Ball Clay with 3 grams of malachite green, we obtain the curve shown in Fig. 6. Now suppose we take 50 grams of any other clay, say, Moore and Munger's Ball Clay, and treat it with the same amount of dye, the amount of dye adsorbed proves to be 2.8779 grams. 2.8779 grams comes on the curve at 43.35 grams Tenn. Ball No. 3, or 90.7 Relative Colloids. That is, it is assumed that clays adsorbing equal amounts of dye contain equal amounts of colloids, and these are expressed in terms of the amount present in Tenn. Ball No. 3.

Column A, Jackson-Purdy Surface Factor, contains numbers assumed to be proportional to the total area of all the particles in a unit weight of clay, and is thus a measure of the fineness of the material. The method was originally proposed by W. Jackson (23) and made more general by Ross C. Purdy (24).

Column B, Cast Air Shrinkage, contains values obtained by casting a clay slip into a plaster of paris mould 10 cm. in diameter, using approximately 50 grams of clay, and giving a test piece about 0.5 cm. thick. A number of precautions are necessary for accurately comparable work, and it is regretted that some of these figures, three years old, do not have the precision of later work (25), (26).

The column of Fire Shrinkage at Cone 8 is put in merely because of its general interest.

In column D has been put the surface concentration of colloids, obtained by dividing the *relative colloids* by the *surface factor*. It is an attempt to express numerically the density of the layer of colloid material that is considered as enveloping the granular material. Theoretically, not the surface factor, but only that portion corresponding to the granular material should be used; but the method for obtaining this information has not yet been worked out. It is assumed that the various clay colloids will differ in their ability to absorb water, and, consequently, in their shrinkage. In column E it is attempted to measure this effect by calculating the specific air shrinkage; for which purpose the *linear air shrinkage* is divided by the *relative colloids*.

The lubricating layer, permitting of motion to the granular particles, is made up of colloids holding water; and in column F, this is estimated as deformability, directly proportional to the surface concentration of colloids and to the specific air shrinkage of these colloids, hence to their product.

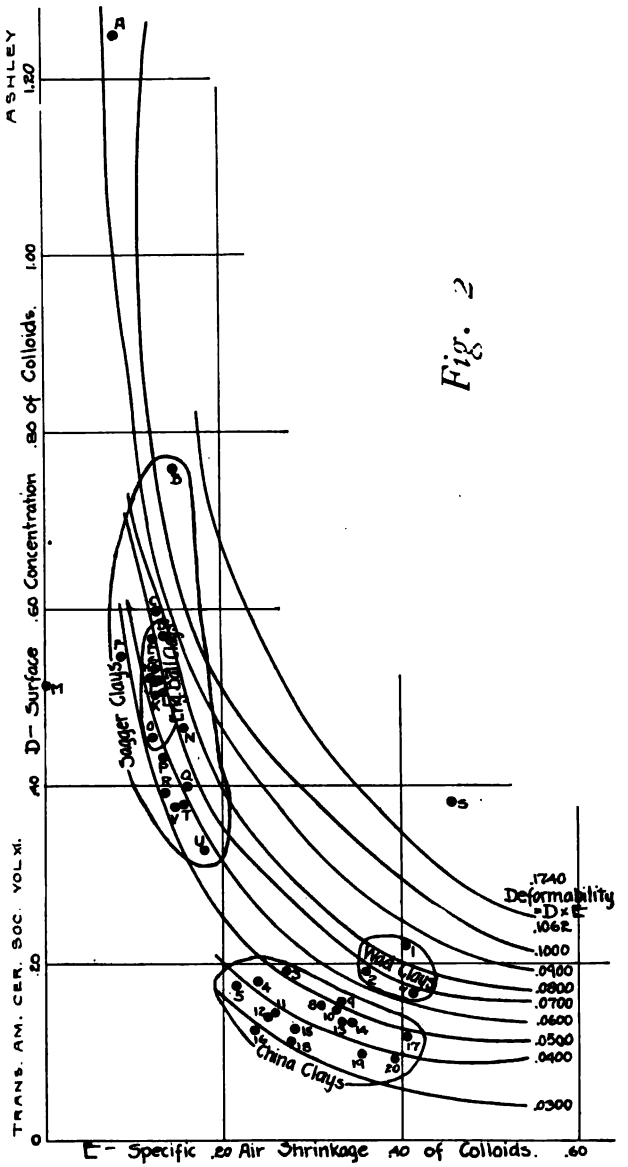

TRANS. AM. CER. SOC. VOL XI.
ASHLEY
1.20
1.00
.80 of Colloids.
.60 Concentration
.40 D- Surface
.20
0
E- Specific .20 Air Shrinkage .40 of Colloids. .60
Jagger Clays
Ball Clays
China Clays
.1740
Deformability
=D×E
.1062
.1000
.0900
.0800
.0700
.0600
.0500
.0400
.0300

Fig. 2

Surface Concentration and Specific Air Shrinkage of Clay Colloids and Their Relation to Deformability.

(Fig. 2.)

A Texas Kaolin
C Prall No. 1 Sagger
D Prall No. 1 Retort
E Knowles No. 12 Ball
F Potters' Supply No. 3 Tenn. Ball
B Mandle-Sant Special Sagger
G Pike's No. 20 Ball
H Ryan No. 1 Sagger
I Paul, Ground Fire Clay
J Mandle-Sant No. 3 Tenn.
K Atlanta M. & C. Co.
L Ken. C. & I. Co., No. 1 Sagger
M Diamond Fire Clay Co.
N Johnson-Porter No. 9 Tenn.
O Moore & Munger Ball
P Excelsior B. C. Co. Sagger
Q Potters' Supply Co.'s Tenn. No. 4
R Edgar No. 8 Sagger.
S Edgar Florida
T Such BB Sagger
V Mandle-Sant No. 11 Tenn.
U Edgar No. 10 Sagger
1 Johnson-Porter Wad
2 Potters' Supply Co. Wad
3 Johnson-Porter UX Sagger
4 Harris, Penland
5 Harris, Bryson
6 Priem Zettlitz Kaolin
7 Mandle-Sant Wad
8 Hall-Georgia
9 Mandle-Sant Tenn. No. 9
10 Johnson-Porter No. 1 Ball
11 Adolph Wh
12 Hammill & Gillespie Al
13 Duncan-White Mt.
14 Poole No. 1
15 Poole BB
16 Moore & Munger HN
17 Sant Bluemont
18 Peach Kaolin Co.
19 Moore & Munger M. G. R.
20 Knowles No. 15

The relations of columns D, E, and F are shown graphically in Fig. 2. It will be seen that Ball and Sagger Clays fall in one group, having colloids of low specific air shrinkage. The china clays fall in another distinct group having low surface concentration of colloids. The wad clays apparently form a distinct group with somewhat greater surface concentration of colloids than the china clays. The Texas and Florida "Kaolins" are distinct from all other clays, and from each other. The two fire clays tested are closely associated with the ball and sagger clays. With finer grinding the resemblance would appear stronger.

Finally in column G an expression is given for plasticity. Both Zchokke (27) and Grout (28) have experimentally determined plasticity as the product of a deformation by the force producing it. Similarly it is here taken as the product of the deformability by the force resisting deformation, assuming that this resistance is exerted by the colloids which are the cementing materials supplying the cohesion of the clay. This is the product of columns C and F, but F is the product of columns D and E, and these represent $\frac{C}{A}$ and $\frac{B}{C}$ respectively; whence $G = \frac{C \times B}{A}$.

Since ordinarily the shrinkage (B) and the surface factor (A) are both highest with high collodial matter (C), it is evident that $\frac{B}{A}$ will approximate a constant, and that plasticity is mainly due to the relative colloids (C). The fraction $\frac{B}{A}$ seems to take care very satisfactorily of the variations in the nature of the colloid matter and of the size of grain.

It will be noted that increased fineness of grain is considered as cutting down the plasticity. It has been the writer's repeated observation that increased fineness of the granular material in a clay or body is a source of weakness and trouble; that, having greater surface, more

colloid matter is required to cement the fine grains together. In the following table the clays are arranged as classified by column G.

Plasticity of various clays.

Texas, "Kaolin"	10.340
SAGGER CLAYS.	
Mandle-Sant, Special Sagger	9.090
Prall, No. 1 Lt. Sagger	7.270
Knowles, No. 12 Ball	6.530
BALL CLAYS.	
Pikes, No. 20 Ball	6.280
Mandle-Sant, No. 3 Tenn	5.960
Johnson-Porter, No. 9 Tenn	5.760
Kenn Cons. & Imp. Co., No. 1 Sagger	5.690
Edgar Plastic Kaolin Co., Florida	5.660
Prall, No. 1 Retort	4.900
Moore & Munger, ball	4.880
SAGGER CLAYS.	
Ryan, No. Sagger	5.790
Atlanta Min. & Clay Co., Ga	4.730
Potters' Supply Co., No. 3 Tenn	4.620
Potters' Supply Co., No. 4 Tenn	4.520
Excelsior Ball C. Co., Sagger	4.200
Such, B. B. Mixture	3.660
Edgar Bros. Co., No. 8 Sagger	3.510
Johnson-Porter, No. 10 Tenn	3.450
Edgar Bros. Co., No. 10 Sagger	2.630
Paul Clay Co., ground fire clay	2.595
WAD CLAYS.	
Johnson-Porter, X Wad	1,867
Johnson-Porter, UX Sagger	1.824
Potters Supply Co., Wad	1.775
Mandle-Sant Clay Co., Wad	1.530
Mandle-Sant Co., No. 9 Tenn	1.473
Johnson-Porter, No. 1 Ball	1.378
CHINA CLAYS.	
Hall Clay Co., G. N. Sagger (Kaolin)	1.335
Priem, Zettlitz Kaolin	1.335
Harris, Penland China Clay	1.117
Adolph, W. H., China Clay	1.104
Harris, Bryson China Clay	1.097
Poole, No. 1 China Clay	1.097
Sant, Bluemont China Clay	.910
Duncan, White Mt. Clay	.903
Poole, B. B. China Clay	.873
Hammill & Gillespie, Al. C.C	.868
Moore & Munger HN China C	.675
Moore & Munger, MGR China C	.647
Knowles No. 15 China Clay	.618
Peach Kaolin Co., China Clay	.556
Diamond Clay Co., ground fireclay	.000

DISCUSSION OF ERRORS.

Various anomalies have to be explained. Experimental errors in elutriation, due to incomplete deflocculation of the clays, have probably made too high the values marked with ? points. In these cases the dyed clay was elutriated. It was found out later that dyeing increases the size of the flocculles, and hence decreases the surface factor. The two No. 3 Tennessee Ball Clays occur on adjacent properties. It is believed that the shrinkage measurements or the surface factors of one or both are in error, the former having been made three years ago for one of the clays, and the latter presenting difficulties in deflocculation. The Mandle-Sant No. 9 Tenn. Ball is much more plastic than its position in the table indicates. Neither UX nor No. 1 Ball is a strong clay, and they are correctly placed. Among the China Clays there is the possibility of the addition of some whitening agent, or of wetting by salt water in transit across the ocean that would interfere with the colloid test. The lowest English Clay on the list, Knowles No. 15, has a very good reputation as a safe clay. The Diamond Clay Company fire clay with finer grinding will have a measureable shrinkage and is capable of being classed with the Sagger clays if so ground. But, as supplied, its shrinkage is less than the possible error of my measurements, and it is correctly placed as to the plasticity in the coarse ground condition.

The maximum errors possible are probably 20 per cent in the case of the surface factor, 1 per cent of the total length for air shrinkage, and 5 per cent for relative colloids. The average errors, however, will not exceed 2 per cent for surface factor, 0.3 per cent for air shrinkage, and 2.5 per cent for relative colloids.

On the whole I am very well satisfied with this table as accurately representing that indefinite collection of properties of clays that we call plasticity.

FUTURE WORK.

The possible disturbing effect of various soluble salts and minerals should be determined.

The rate of deterioration of standard solutions should be studied.

My studies have been confined to high grade clays. A wider range of materials should be studied. I have collected samples of the various bodies used in the ceramic industries, and intend to ascertain whether definite numerical limits can be given for the plasticity required by each. It is also intended to study the process of ageing clays, as this method will permit measurements of the progressive increases in plasticity.

It is intended to formulate a field test for plasticity that will give an idea whether clay is worth more accurate investigation.

Seger (29) has noted in several places that there seems to be a close relationship between the amount of soluble salts in a clay and its plasticity. Purdy and Moore consider it "an exceedingly probable assumption that it is the influence of the adsorbed salts that gives to a clay its plasticity" (30). It is possible or very likely that in the malachite green test, the color base is exchanged with the bases that stabilize the gel and with the bases of the soluble salts present, and that the oxalates of lime, etc., are precipitated. It is possible that by the use of a dye having its color base united with hydrochloric acid, we may secure an elegant means of studying the soluble salts in clay, as Hirsch's work with aluminum chloride indicates the feasibility of such a procedure.

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DISCUSSION.

Mr. Purdy: Having had the privilege of reading Mr. Ashley's paper in advance of this meeting, I have, at the request of our Secretary, prepared a discussion of it:

The theory of the cause of plasticity in clays, which appears to be most tenable, is that of adsorbed or otherwise held salts, which on addition of water form a viscous solution about the grains, resulting in an enveloping liquid media of high surface tension. I propose to first set forth the facts on which I base this theory, then present the physical conception involved, and lastly to show the parallelism of this with the colloid theory.

THE CLAY GRAINS.

It is commonly known by paving brick manufacturers that some shales require inordinate pugging before they develop sufficient plasticity to permit the production of a perfect bar in the die of the brick machine. In fact it is not uncommon to see a battery of two pug-mills thru which the clay must pass before it enters the brick machine proper. In the brick machine the clay receives further pugging before it issues as a bar from the die. It is also not uncommon to hear the manufacturers claim that they cannot pug clay sufficiently unless they use hot water.

Not all manufacturers have to resort to this extra care in the pugging process, for some shales develop plasticity with sufficient readiness to allow them to emerge from a single pug-mill in a workable condition.

This difference in the working properties of shales is considered to be due to the fact that the grains of clay are cemented by substances that differ in their solubility in water. It is now well known that soils and clays contain soluble salts that are adsorbed by, or, to use a more homely expression, smeared over the particles, and are not easily extracted by water. It has been learned by experiment that clays can take on or adsorb soluble salts from solutions and so retain these salts that they cannot again, under ordinary conditions, be dissolved from the clay. It is considered that these adsorbed salts are the cementing bond in the clay grains.

The amount of water used in the pugging of the shales is not sufficient to dissolve or loosen all of the cementing salts in a clay, even by continued pugging, so that at best, only a portion of the clay particles are separated from one another; but the manufacturers must continue pugging until a sufficiently large number of grains are separated to form a slippery medium, by virtue of which the unslaked or undisintegrated bundles of particles can slip past one another freely enough to permit a flowage of the mass under pressure. The difficulty encountered by manufacturers in breaking down the cementing bond in shales is increased many-fold when an attempt is made to disintegrate a clay into its ultimate grains, as in the mechanical analysis. While it is comparatively easy to obtain separation of the *loose-grained clays* in the laboratory and in the factory, it is obvious that it is not possible to obtain a similar separation of the particles of the *hard rock-like clays* in the factory, and very difficult to obtain much more than an approximation of ultimate subdivision in the laboratory. It is owing to this indefinite degree of solution of the natural bond in pugging that we have, in the case of shale bricks, a discordant

relation between the porosity of the brick and the fineness of grain, as contrasted with the seemingly concordant relation in the case of bricks made from Loess clays.

Analytical Proof: Because in the mechanical analysis the coarser grains have been reported as sand and the finer particles as silt and clay, not a few have taken it for granted that clay substance cannot be present in the large grains after the clay has been thoroughly disintegrated in water. Grout[1] has shown, however, that this conception is entirely erroneous. In Table I is given the amount of clay substance that he obtained first, from the rational analysis; second, calculated from ultimate analysis; and, third, obtained from mechanical analysis.

Table I.

Showing the discrepancy in the reported "clay substance" in clay, by the three methods of determination now in vogue.

Specimen Number	Rational Analysis	Calculated Kaolin	Mechanical Analysis
4	67.23	52.30	11.80
17	36.80	26.39	36.85
41	72.26	41.65	63.70
62	70.48	41.14	59.70
76	42.41	31.50	33.35

These data not only show the discrepancy in the chemical methods of determining the mineralogical constitution of clays, but also that a very considerable part of the alkali is not combined as feldspar but either as a part of minerals soluble in hot sulphuric acid or as free alkali. They show by the figures in the third column that a goodly portion of the clay substance is bound with other minerals forming the coarser grains.

(1) Geo. Surv. W. Va., Vol. III., p. 26.

Mr. Grout has also given results of the chemical analysis of a composite mixture of the several grades of fineness obtained from 16 samples of clay as follows:

Table II.

Constituents.	.00 to .001	.001 to .005	.005 to .02	.02 to .15	.15 up
SiO_2	44.03	54.54	70.30	81.16	73.63
Al_2O_3	28.16	23.00	16.04	9.76	13.01
Fe_2O_3	7.94	5.91	3.21	2.13	4.71
FeO	0.99	0.99	0.63	0.40	0.18
MgO	1.36	1.02	0.80	0.39	0.48
CaO	0.76	0.82	0.72	0.31	0.47
Na_2O	0.00	0.29	0.45	0.56	0.00
K_2O	3.05	3.31	2.14	1.78	0.93
H_2O	2.80	1.10	0.56	0.35	0.87
Ignition	10.86	7.79	4.33	2.59	4.40
TiO_2	0.84	1.12	1.08	0.78	0.60

In this he has proved conclusively that the "clay substance" is present in every grade of fineness. His own conclusions from these analyses are, "The silica percentage is higher in the coarser portions, where it probably is present in the form of sand or quartz. Alumina is higher in the finer material, but total fluxes are also higher, so that the finest particles are not the purest kaolin."

In order to make a clearer analysis of his data, they have been calculated into molecular equivalents as given in the following table: —

Table III.

Grades of Fineness	SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	Na_2O	K_2O	TiO_2
0.00 to 0.001.....	2.66	1.00	0.18	0.050	0.12	0.050	.....	0.12	0.040
0.001 to 0.005.....	4.03	1.00	0.16	0.060	0.11	0.060	0.02	0.16	0.060
0.005 to 0.02.....	7.45	1.00	0.13	0.060	0.13	0.080	0.05	0.14	0.090
0.02 to 0.15.....	14.14	1.00	0.14	0.590	1.02	0.580	0.94	0.19	1.020
0.15 up	9.62	1.00	0.02	0.002	0.01	0.007	.....	0.008	0.006

A review of Grout's mechanical analysis of the West Virginia clays discloses the fact that he made 26 determinations: —

6 Plastic fire clays, pp. 160, 162, 163, 233 and 251.
1 Flint fire clay, p. 218.
7 Shales, pp. 249, 251, 242 and 262.
10 River clays, pp. 263, 265, 270, 272, 274 and 276.
1 Glacial clay, p. 265.
1 Residual surface clay, p. 200.

It is assumed, therefore, that the samples, the analyses of which are given in Table II, are composites of the several grades of grains from the above clays. Being in most cases very impure clays, a study of the possible mineral make-up of each grade will have to be largely based on hypothetical assumption(1). Such a study, however, will aid us to understand the constitutional make-up of clays.

(1) The writer while using these assumptions is aware that they are far from satisfactory in that they no doubt lead to conclusions that are not correct. They are, however, in common use and are the only ready chemical means we have with which to study the constitution of clays.

On the assumption that all the alkali is present as a RO in orthoclase feldspar, the molecular ratio and ratio by weight of koalin, feldspar and quartz present in each grade would be as follows: —

Table IV.

Showing possible mineral constitution of the several grades of grains in impure clays.

Grade	Molecular Ratio			Weight Ratio		
	Kaolin	Feldspar	Quartz	Kaolin	Feldspar	Quartz
0.00 to 0.001.....	0.880	0.120	0.18	10	2.90	0.08
0.001 to 0.005....	0.820	0.180	1.25	10	4.70	3.50
0.005 to 0.02.....	0.810	0.190	4.69	10	5.10	13.50
0.02 to 0.15.....	.....	1.000	8.14	.....	10.00	8.00
0.15 up	0.992	0.008	3.62	10	0.18	8.50

These data show that clay substance is to be found in all of the grades of fineness, in the coarsest as well as the finest. They also show that more than 50% of the coarsest group, or as it is customarily called, "coarse sand", may be kaolin, or is at least kaolinitic in composition.

As a further analysis of the probable mineral make-up of clays, Grout's data will be discussed by groups. In this only the most common and abundant minerals known to occur in clays are considered.

Coarsest grade (0.15 mm.): — This grade of grain, even if all the alkali is considered as being present as a constituent part of feldspar grains, would be assumed to be composed almost entirely of non-disintegrated kaolin and quartz grains. Only in one case, however, does Mr.

Grout speak of the physical character of the grains of this grade. In this particular case the clay examined is a shale.

"The 12.9 per cent (referring to coarse sand grade) on 3 mm. screen was mostly flat scales of shale, about 5 mm. in size, of red and greenish color." The total absence of similar description of this grade in the other twenty-five samples justifies the conclusion that the grains of this grade were flat or scale-like only in this one sample. If this conclusion is true, then it is fair to assume that either the kaolin scales are present in undissolved bundles devoid of characteristic shapes, or these grains are not composed of kaolin but some other aluminum compound like gibbsite, etc. They are large enough to be identified under the microscope.

On the other hand, it is hardly possible that grains of feldspar of this size could remain unaltered in these old river clays that have been elutriated, mixed and moved by fresh waters possibly for ages. There is justification for the assumption, therefore, that these coarse grains are bundles of kaolinite, feldspar, and quartz grains cemented together so tightly by some salt that they resist disintegration by water. If all the alkalies had been present as constituent parts of feldspar grains of this size, the feldspar crystals could have been easily recognized under the microscope as cubical grains. They must have been in part constituents of the cementing salts.

H. B. Fox, in the ceramic laboratories of the University of Illinois, separated the grains of a shale and a glacial clay into the several grades of fineness, and found that all the grades possessed a plasticity that varied directly with the fineness of grain, and that the coarse grains which could not be disintegrated by 20 hours of constant shaking in water, when broken down in a mortar, developed plasticity that increased as the size of the grains decreased, until when the coarse grains had been reduced to an impalpable powder they developed a plasticity nearly equal to that exhibited in the finest grains that had been

separated from the original sample, showing, it is believed, that the coarser grains comprised materials similar in every respect to those in the fine grains, but cemented in such a way that they withstood successfully the disintegration treatment.

(0.02 to 0.15) Grade: It is highly improbable that this grade contained no kaolin or clay substance, but such would have to be the case if all the alkali was present as a constituent part of the orthoclase feldspar grains. Nor could the alkalies be present in this case as easily soluble salts, for the larger part of the alkaline salts would have been dissolved, carried in solution, and would affect only the finest grades. If the feldspar was oligoclase and not orthoclase, then the 0.5 equivalents of the alumina could be considered as being derived from kaolin.

Altho there is no statement made as to the presence of mica in the clays from which these grades of grains were obtained, Mr. Grimsley states that it is a very common constituent of the West Virginia clays. On the assumption that the alkali is present wholly or in part as a constituent of mica, let us consider what we would have.

Stull[1] gives as the chemical formula of common muscovite mica the following:

$$\left.\begin{matrix} 0.1243\ CaO \\ 0.1103\ MgO \\ 0.3280\ K_2O \\ 0.0929\ Na_2O \end{matrix}\right\} \begin{matrix} 1.00\ Al_2O_3 \\ 0.1857\ Fe_2O_3 \end{matrix} \left\{ 6.399\ SiO_2 (0.974\ H_2O) \right.$$

Comb. Wt. 582.167

On the assumption that the alkali in this grade is derived wholly from muscovite mica of the composition given by Stull, the mineral constituents of this grade of grain might be proportioned as shown by the following calculations: —

(1) Trans. A. C. S., Vol. 4 p. 258.

	SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	Na_2O	K_2O	TiO_2
	14.14	1.00	0.14	0.59	1.02	0.58	0.94	0.19	1.02
.57 Eqv. Mica.....	3.65	0.57	0.11	.....	0.06	0.07	0.05	0.19	.....
	10.49	0.43	0.03	0.59	0.96	0.51	0.89	.....	1.02
.43 Eqv. Kaolin....	.86	0.43	.....	.....	.....	.....	.....	.....	.....
	.63						0.89		

0.57 Eqv. Mica x 582.167 = 331.835 or by proportion 30.0
0.43 Eqv. Kaolin x 258 = 110.940 or by proportion 10.0
0.63 Eqv. Silica x 60 = 37.800 or by proportion 3.4

In this case, the formula most favorable to the supposition that all the K_2O is present in the form of mica has been taken. If the theoretical formula K_2O 3 Al_2O_3 6 SiO_2 2 H_2O had been taken, there would have been either considerable K_2O to account for in some other way, or return to the original hypothesis that this group contained no kaolin. Either supposition leaves considerable alkali unaccounted for which, as has been pointed out, could not possibly be present in an easily soluble form, and yet not wholly as a constituent of feldspar or mica.

The supposition, therefore, that this grade is composed in part of kaolinitic grains cemented together by some alkaline salts, finds support in any plausible assumption that may be made.

(0.005—0.02) and (0.001—0.005) Groups: If the kaolin grains in these groups were in their natural condition, i. e., flat plate-like crystals, they should, theoretically, be visible through the microscope. This evidently was not the case. Beyer and Williams [1] say: "While it is next to impossible to make out much concerning the crystalline character of the minerals, it is also difficult, because of their minute size in most secondary clays, to say anything regarding their shape." In other words, the shape of the grains is irregular and non-conformable one with another, i. e., bundles of still smaller grains. If in these grades there is as much kaolin as is shown in Table

[1] Iowa Geol. Surv., Vol. XIV., p. 94.

IV, its grains must be, to a very great extent, in bundles or they would have been recognized under the microscope. If the feldspar or mica is present in such amount and size of grain, as the calculated data suggest, their grains ought to be detectable with the aid of the microscope. Such, however, is not the case. The supposition, therefore, that all the alkalies of these two grades are there as constituent parts of feldspar and mica is certainly untenable.

(0.000—0.0001) Grade: The molecular composition of this group is certainly very instructive. That in such heterogeneous mixtures as shales and river clays the finest particles are found to be composed in the main of kaolinitic grains is certainly astonishing. If the bases present, as shown in Table III, are considered as being present as soluble salts that were either originally present in the clays or in part introduced during the process of analysis, (a most plausible assumption) then there would remain but one conclusion, that is, that the finest insoluble grains are almost entirely kaolinitic in composition.

Taking data given by Grout, it was calculated that if all the soluble salts originally in the clays were in the finest group, they would amount to 2.7 per cent of the weight of that group. The 2.7 per cent, together with the soluble salt introduced during the process of analysis from glassware, water, atmospheric dust, etc., would account for nearly all of the alkali in the finest grade. It is not mere assumption, therefore, that the finest particles in clay, contrary to Grout's statement, are the purest kaolin grains.

In the course of a research on paving brick clays* there was much speculation as to the number of these submicroscopic kaolin grains in the various shales. This was readily ascertained as follows: By dividing the percentage amount of the group (0.001 to 0) by 100, and considering that as being a part of 1 milligram of the sample, (for the size of the particles is in millimeters) then divid-

*State Geological Survey of Illinois. Bull 9.

ing this amount by the specific gravity of the clays, a figure is obtained that represents the sum total volume in cubic millimeters of the particles comprising the group. Considering 0.0005[1] as the mean diameter of the particles, by the formula $\frac{Pi0^3}{6}$ the volume of each particle is found to be 654×10^{-13} cubic millimeters. Then for each clay, by dividing the total volume of the particles by the volume of one particle, the number of grains per milligram of the sample will be obtained. By multiplying the number of grains in one milligram by 1,000 there would be obtained the number of grains in 1 gram; or by multiplying by 352,740 there would be obtained the number of grains of this size in 1 oz. of the whole sample. In this way Table V was calculated.

Table V.

Number of grains of group (0.001 to 0) in—

Sample No.	1 gram of the clay.	1 oz. of the clay.
K 1	560.0 trillions.	197,534 trillions.
K 2	829.0 trillions.	292,421 trillions.
K 3	794.0 trillions.	280,075 trillions.
H 23	1,588.7 trillions.	560,398 trillions.
H 21	1,940.0 trillions.	684,315 trillions.
K 6	440.0 trillions.	166,205 trillions.

These figures although beyond the limits of perception of the human mind, are not larger than the figures representing the countless germs that bacteriologists claim can exist in a single drop of a fluid. Startling as this data appears to be, it cannot be other than true if the analytical results of the mechanical separation are correct.

(1) Cushman, Jour. Am. Chem. Soc., Vol. XXIX, No. 4, p. 589, has shown the inaccuracy of assuming that the mean diameter of a group of particles can be obtained by averaging the extreme diameters of that group.

In clays, therefore, we have, constituting the larger grains, mineral aggregates cemented together and in the smallest grains nearly pure clay substance.

WATER REQUIRED TO DEVELOP PLASTICITY.

Excess Water: A moment's reflection will make plain that in order to have a development of plasticity there must be water in excess of that required to fill the pores that are present when the clay mass is dried. The amount of this excess water in several shales is shown in Table VI.

Table VI.

Sample Number	Plasticity water	Porosity	Sp. Gr. of Clay	Per cent by weight of water required to fill the pores	Per cent or wt. of excess water required for plasticity
K-1	14.9	26.0	2.67	11.6	3.3
K-2	16.77	25.7	2.56	11.9	4.8
K-3	16.82	25.6	2.69	11.4	5.4
K-4	16.27	27.8	2.67	12.6	3.6
K-5	13.06	25.4	2.65	11.3	1.8
K-6	17.03	28.9	2.66	13.2	3.8
K-7	17.57	27.9	2.64	12.7	4.9
K-8	14.4	25.2	2.69	11.1	3.3
K-9	13.4	26.1	2.70	11.5	1.9
K-10	19.6	25.4	2.69	11.2	8.4
K-12	13.35	18.3	2.67	7.7	5.7
K-13	16.3	28.3	2.70	12.7	3.6
K-14	13.6	24.5	2.64	10.9	2.5
S-1	17.2	23.0	2.64	10.1	7.1

Table VI.—Continued

Sample Number	Plasticity water	Porosity	Sp. Gr. of Clay	Per cent by weight of water required to fill the pores	Per cent or wt. of excess water required for plasticity
S-2	16.6	26.4	2.72	11.6	5.0
R-1	13.4	17.8	2.73	7.9	5.5
R-2	13.0	24.0	2.72	10.4	2.6
R-4	13.2	21.8	2.72	9.3	3.9
B-II	17.7	26.9	2.67	12.1	5.6
G-II	11.8	22.4	2.70	9.6	2.2
H-II	16.5	20.7	2.68	8.8	7.7
I-II	14.4	18.9	2.67	8.0	6.4
J-II	16.5	24.2	2.70	10.5	6.0
L-II	16.4	24.5	2.70	10.7	5.7
H-16	16.2	27.8	2.70	12.4	3.8
H-17	16.6	19.0	2.60	8.2	8.4
H-20	18.3	23.9	2.72	10.3	8.0
H-21	18.0	21.6	2.72	9.2	7.8
H-23	21.4	24.9	2.63	11.1	10.3
H-24	12.8	14.5	2.66	5.9	6.9

Molecularly Attracted Water: A theory for the cause of plasticity has been advanced which involves the notion of a molecular attraction between the clay particles and the water. To properly appreciate this conception of the cause for plasticity, suppose clay to be blunged into the form of a slip, as is the practice of the potter before casting a vase. In this slip or fluid condition each grain is surrounded or enveloped by a film of water. If the volume of water is large compared with the total volume of clay

particles, the mass will behave in every respect like a fluid; indeed, as will the turbid water of the Mississippi. Suppose that, by evaporation, or absorption by a plaster mold, the volume of the water be decreased. The clay particles will be brought closer and closer to one another, causing the mass to pass from a fluid state through various stages of consistency until it assumes a stiff plastic condition; a process to be observed in mud roads after every rain. When in this stiff condition the particles still have an envelope of water or, in other words, they are still suspended in water just as truly as they were when the mass was more of a fluid. But, owing to their proximity, it is assumed by those advancing this theory of plasticity, that they are held in position by the molecular attraction which each particle of clay substance exerts on the other.

Text books on physics give as an "expression" for the force of molecular attraction between two molecules, M and M^1, $MM^1f(r)$. "All that is known about this function of r is that it is very large for insensible distances, that it diminishes very rapidly as r increases and that it vanishes while r is still very small. The maximum value of r at which molecular action ceases is estimated by Quincke to the 0.00005 mm. If the particles then were 0.00005 mm. or 0.00002 inches apart, they would be at the extreme distance through which molecular attraction can possibly operate. Grout[1] says, however, "Now a simple calculation, based on the mechanical analysis of the clays, will show that the amount of water needed to place a film 0.00005 mm. thick around each grain is often nearly equal to the amount added in tempering, so that in ordinary plastic clay, it is necessary to consider practically all the water as being under this influence."

Grout bases his reasoning on the following calculations: He found that his "mechanical analyses frequently show a large percentage of grains below 0.001 mm. in di-

[1] Jour. Am. Chem. Soc., Vol. XXVII, No. 9, Sept., 1905.

ameter, also from 0.001 to 0.005 mm. The average diameter of grains below 0.001 mm. is 0.0005 mm. If these are considered spherical and of specific gravity 2.5, it would require 25.5 per cent by weight of water to place around each grain a film 0.00005 mm. thick."

On making these same calculations the following was obtained:

Vol. of sphere $= \frac{\pi D^3}{6}$

Given diameter of sphere 0.0005.

$\frac{\pi}{6} \times 0.0005^3 = 6545 \times 10^{-14}$ volume of clay sphere.

Diameter of sphere plus water film=.0005+.0001 or .0006.

$\frac{\pi}{6} \times 0.0006^3 = 1131 \times 10^{-13}$ volume in cu. mm. of sphere of clay plus water.

Reducing these figures for the sake of convenience to

0.6545=volume of clay sphere,

1.131 =volume of clay plus water sphere,

0.6545÷1.131=0.5775, part of unit volume of clay plus water sphere occupied by the clay.

1.00 — .5776=0.4224, part occupied by water film.

Given specific gravity of clay=2.5.

Since in the metric system Vol. x Sp. Gr.=Weight.

0.5775 x 2.5=1.4540 parts by weight of clay.

0.4224 x 1.0= .4224 parts by weight of water.

1.8764 total weight.

0.4224÷1.8764=0.2251, parts by weight of water in a unit volume of clay plus water film, or 22.5 per cent.

This calculation, so far as the validity of Grout's argument is concerned, checks his results.

It must be admitted by the supporters of Grout's molecular attraction theory for plasticity, that he used but a portion of a very fine-grained clay on which to calculate

his demonstrating example. If he had taken into consideration the data for the sample of clay as published by him instead of only those for the finer portions, quite different results would have been obtained as is shown in Table VII.

The calculations by which the data in the following table were obtained are:

(a) Volume of clay sphere $\frac{\pi D^3}{6}$ where D is the mean diameter of the range in each group of the mechanical analysis.

(b) Volume and weight of water film $\frac{\pi(D-0.0001)^3}{6} - \frac{\pi D^3}{6}$.

(c) Weight of dry clay particles as given in the mechanical analysis.

(d) Total or collective volume of spheres in each group: Weight given ÷ Sp. Gr. of the clay.

(e) Number of spheres in each group per unit volume: Total volume of each group ÷ volume of clay sphere or $\frac{d}{a}$.

(f) Weight of water film surrounding the sphere in each group of the sample: Weight of water film times the number of spheres or $e \times b$.

(g) Sum of water required to give each particle in the sample a water film of prescribed thickness.

Table VII.

SAMPLE	Sp. Gr.	Total dry weight of clay particles by analysis	Total weight of water films by calculation	Analyst	Reference to data used and explanatory notes
S. C. Besley, top clay (1)	2.34	0.9844	0.0165	Williams...	pp. 116 and 123, Ia. Geol. Surv. Vol. XIV.
S. C. Besley, middle clay	2.32	0.9834	0.0219	..do	Williams' first group was termed "about o.1mm."
S. C. Besley, bottom clay	2.40	0.9819	0.0263	..do	In this group the mean diameter of the particles was assumed to be o.175mm.
Dale Brick Co	2.44	0.9857	0.0320	..do	
Gethmann Bros.	2.41	0.9739	0.00254	..do	
Clarksburg fire clay (2)	2.52	0.9880	0.0393	Grout	pp. 65 and 251 W. Va. Geol. Surv., Vol. III
Bridgeport stoneware clay (2)	2.35	0.9870	0.1750	..do	pp. 65 and 162 W. Va. Geol. Surv., Vol. III. Attracted water=15+per cent.
Charleston river clay (3)	2.66	0.987	0.1009	..do	pp. 65 and 200 W. Va. Geol. Surv., Vol. III
Parkersburg pottery clay	2.58	0.984	0.1043	..do	pp. 65 and 160 W. Va. Geol. Surv., Vol. III
K-1 Alton, Ill. (4)	2.66	1.045	0.0356	Krehbiel and Moore..	
K-2 St. Louis, Mo.	2.56	1.021	0.0491		
K3 Albion, Ill.	2.686	1.002	0.0475		
K-4 Springfield, Ill.	2.67	1.037	0.0703		
K-5 Edwardsville, Ill.	2.65	1.028	0.0390		
K-6 Galesburg, Ill.	2.66	1.027	0.0320		
K-7 Streator, B. B. Co.	2.636	1.037	0.045		
K-8 Veedersburg, Ind.	2.702	1.008	0.029		
K-9 Crawfordsville, Ind.	2,702	1,008	0.029		
K-10 Terre Haute, Ind.	2.69	0.979	0.0804		
K-11 Brazil shale	2.659	1.013	0.0467		
K-12 Brazil fire clay	2.669	1.021	0.0533		No. 2 fire clay.
K-13 Clinton, Ind.	2.71	1.048	0.0479		
K-14 Western P. B. C., Danville	2.72	0.9899	0.0348		
R-1 Nelsonville, O.	2.73	1.023	0.0519		No. 2 fire clay.
R-3 Canton, O. (Imperial)	2.66	1.043	0.041		
R-4 Canton, O. (Royal)	2.72	1.023	0.0902		
I-H Caney, Kan.	2.67	1.013	0.0670		
G-11 Coffeyville, Kan.	2.71	1.045	0.0463		
H-18 Sterling, Ill.	2.67	1.042	0.0593		
H-20 Savanna, Ill.	2.72	1.031	0.0739		
H-21 Galena, Ill.	2.72	1.029	0.10301		
H-23 Carbon Cliff, Ill. (shale)	2.63	1.027	0.0867		

(1) The Iowa clays are loess.

(2) Stoneware or No. 2 fire clays.

(3) Alluvial clay.

(4) The Illinois clays are shales in every instance except K-12 and R-1.

In Table VII there is but one instance, that of the West Virginia stoneware clay, in which the amount of water molecularly attracted even approached that required to develop plasticity. In many instances it does not greatly exceed the hygroscopic water that the clay would retain when dried in open rack dryers. In fact the maximum amount of water which Grout admits could be so molecularly attracted, agrees quite closely with the water which in Table VI is shown to be in excess of that required to fill the pores. While Grout's statement of the facts in this case has been proved incorrect, further investigation has found an apparent relation between the molecularly attracted water and "excess water".

Relation between Excess Water and Fineness of Grain: The calculations of the so-called "molecularly attracted water" was based on the size of grains. The calculations for the amount of "excess water", however, did not involve the size of the grains. It is of interest, therefore, to compare the data for excess water and size of grain as expressed by the surface factor.

In the following table are the mechanical analysis of shales:

Table VIII.

Sample Number	1 m m mean diam. 1.25	1 m m mean diam. 0.5.	0.1-.01 mean diam. 0.05.	.01-.001 mean diam. 0.005.	.001-0 mean diam. 0.0005.	Total	Surface factor
K1	7.27	6.53	56.07	24.86	9.76	104.51	256.
K2	1.07	1.23	66.24	19.63	13.90	102.09	331.
K3	1.50	2.41	57.15	25.14	13.96	100.18	341.
K4	1.40	1.74	48.87	29.41	22.24	103.68	514.
K5	6.38	1.46	60.57	22.93	11.43	102.80	287.
K6	1.24	1.83	65.83	25.98	7.77	102.66	221.
K7	1.35	3.75	60.87	25.89	11.81	103.69	300.
K8	9.66	6.90	48.46	25.40	10.05	100.50	262.
K9	11.39	1.55	65.50	14.72	7.63	100.80	195.
K10	1.08	2.42	24.62	44.29	25.52	97.91	604.
K11	5.36	3.76	43.74	35.45	12.94	101.26	339.
K12	4.49	2.88	40.51	38.82	15.32	102.04	403.
K13	1.82	1.35	46.74	41.73	13.15	104.80	356.
K14	14.23	6.31	42.75	26.03	9.67	98.99	254.
R1	2.16	6.51	38.70	39.32	15.53	102.25	397.
R3	11.69	6.30	52.90	21.60	11.79	104.29	291.
R4	10.15	2.84	49.32	29.13	10.85	102.31	275.
I-11	4.64	3.81	45.50	25.94	21.40	101.31	489.
H18	13.05	17.71	27.57	26.58	19.22	104.16	444.
H20	1.92	2.75	42.01	32.47	23.97	103.13	553.
H21	0.34	0.80	24.34	42.77	34.62	102.80	783.
H23	1.80	2.86	29.95	40.82	27.30	102.74	634.
G2	13.17	2.47	52.57	20.57	15.72	104.52	366.

In the accompanying Curve is shown the relation between excess water and surface factor, and between molecularly attracted water and surface factor.

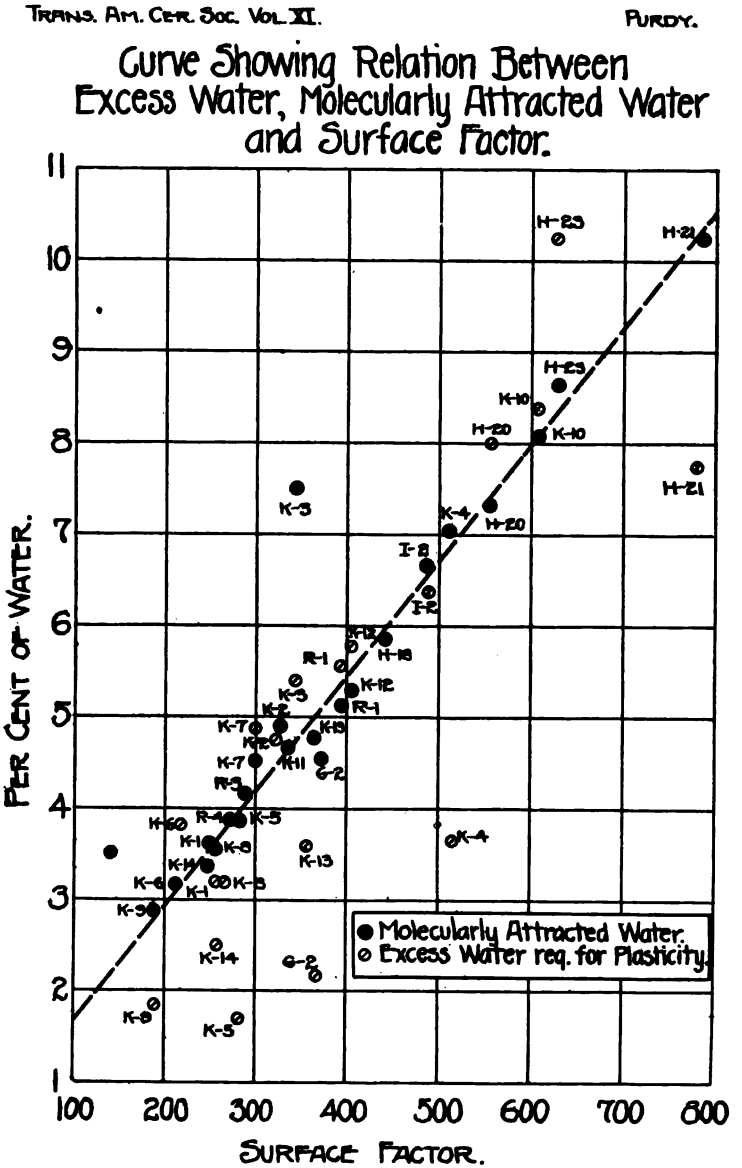
The straight line curve drawn from data for molecularly attracted water and surface factor was expected. Data for both these items are based on the volume and quantity of grains and hence are of the same order.

That the "excess water" data, which are obtained independently of any consideration of the grains as well as from formed masses, should when plotted co-ordinately with surface factor, describe a straight line curve that coincides with that for excess water, is most significant. This close coincidence argues strongly the idea that in excess of that required to fill the pores, there must be sufficient water to furnish each grain its water envelope by which, and in which, conditions are rendered favorable for the development of plasticity.

DEVELOPMENT OF PLASTICITY IN THE PRESENCE OF WATER.

Whatever may be the fundamental cause of this phenomenon we call plasticity, it is certain that it is manifested only when water is present. It has been shown that mere molecular attraction between the clay grains and the water molecules is not sufficient to account for plasticity. There must, therefore, be factors other than molecular attraction that become operative in developing this property, which, when water is not present, may be said to be latent. Since it is the presence of water that makes the development or expression of plasticity possible, it is important that we consider some of the fundamental and well-known hydrostatic forces.

There are at least four forces operating on the water in a plastic mass of clay: First, gravity, or the weight of the water itself; second, surface tension, which is due to attraction (cohesive) between the molecules of water themselves; third, molecular attraction (adhesive) be-


TRANS. AM. CER. SOC. VOL. XI.
PURDY.
Curve Showing Relation Between Excess Water, Molecularly Attracted Water and Surface Factor.
PER CENT OF WATER.
SURFACE FACTOR.
100
200
300
400
500
600
700
800
1
2
3
4
5
6
7
8
9
10
11
Molecularly Attracted Water.
Excess Water req. for Plasticity.

tween the water molecules and the mineral particles in the clay; and fourth, surface pressure, which is the opposite of surface tension.

Gravity: Surface tension, or the contracting power of any exposed water surface, may act with gravity or against gravity, depending upon circumstances. Molecular attraction between the mineral and water molecules always acts in opposition to gravity. Since, as can be shown, the conditions of capillarity in a mass of clay compressed into the form of a brick is such as to make surface tension the very much greater force, and operating in opposition to that of gravity, gravity will not be considered as one of the component forces in our problem. If we were dealing with "slips" or even soft mud mixtures, the force of gravity would have to be considered.

Molecular Attraction: Milton Whitney[1] says: "The potential of a single water particle is the work which would be required to pull it away from the surrounding water particles and remove it beyond their sphere of attraction. It is the total attraction between a single particle and all other particles which surround it." It is called by some "molecular attraction".

Surface Tension: Because it has particles adjoining it only on one side, i. e., molecular attraction is affecting it only from one side, the potentiality of a water particle on the surface is, according to Whitney's definition, only one-half that of a particle in the center of a drop. That things tend to move from points of low to points of high potential is a well-known law of physics. The particles on the surface, will, therefore, strive to get to the interior of the drop. The results will be surface tension.

Looking at this proposition from the mechanical point of view, the force of molecular attraction operating on the surface particles, is effective along lines that extend from the center of each particle, to the center of the surrounding particles. Since the particle on the surface of a drop of

[1] U. S. Dept. of Agr., Weather Bureau Bull. 4, p. 19.

water is under the influence of other particles only from one side, the several lines of force would extend radially from its center to the center of adjacent particles, having as a resultant, a line of force extending from the center of the surface particle to the center of the mass.

Surface Pressure: Suppose that instead of a drop we have the same mass of water surrounding a solid particle as a film, say, 0.0005 mm. thick. We would have in this system two combating forces, first, molecular attraction of water molecules for each other, causing a pull on all water particles toward the center of the film, creating a tension on the outside surface as well as on the surface contiguous to the solid particles; second, attraction between the molecules of the solid particles and those of the liquid, tending to create a tension only on the outer surface of the film.

Consider the water between four solid particles as shown in the following figure as having a potentiality less than that of the solid particles.

All water particles will press outward toward the solid particles along the resultant lines of force as shown in Fig. II. In this case instead of tension we would have a pressure. This pressure is known as surface pressure.

If on the other hand, the water had a potentiality that was greater than that of the solid particles, the resultant forces of attraction would be toward the center of the liquid mass as shown in Fig. III.

The practical conclusion from the above discussion of greatest interest, in connection with plasticity, is that when the surrounding fluid has the greater potentiality, flocculation, or drawing together of the solid particles will result. When the solid particles have the greater potentiality, deflocculation or separation of the solid particles will result. Citations have been presented by Mr. Ashley showing that clays can be flocculated, or deflocculated, depending upon the material carried in solution by the water used in tempering.

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FIG. II.

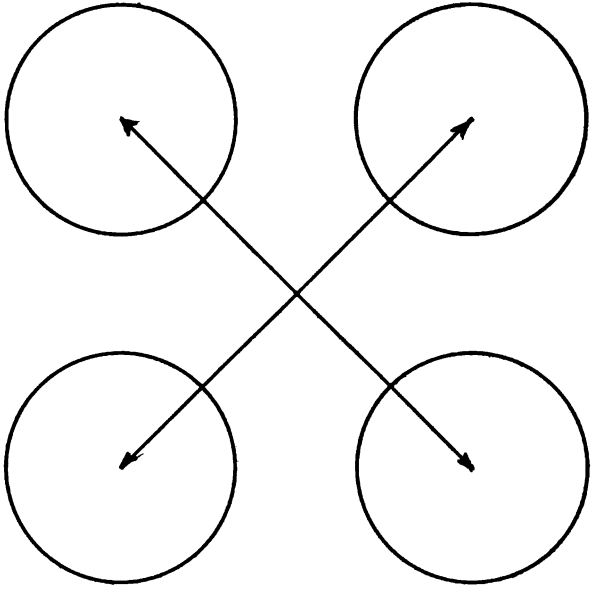

Diagram showing operation of forces causing surface pressure.

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FIG. III.

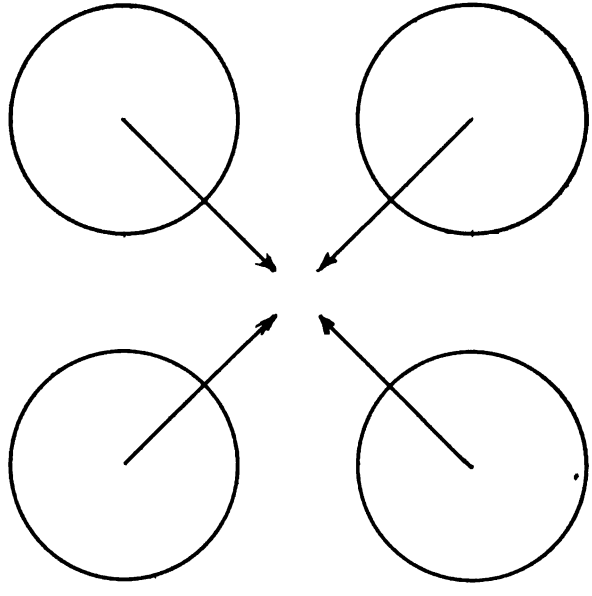

Diagram showing operation of forces causing surface tension.

Solutions causing deflocculation: Johnson, in "How Crops Feed," cites a great many instances where solutions of organic compounds have caused deflocculation of soils. Acheson[1] has shown that tannin will deflocculate clay so thoroughly that when a thin slip of clay suspended in a solution of tannin is poured onto a filter paper the water passing through will be very turbid. Ammonia is used in the water when a clay is being disintegrated preparatory to mechanical analysis. Petroleum is greedily absorbed by the clay because of its low surface tension or potentiality, being held between the minute grains of clay by virtue of the higher potentiality of the clay grains. Whitney[2] has shown that cotton-seed meal, tankage, etc., have similar effects.

Points to be noted in regard to solutions are: 1. Solutions of organic compounds have a much lower surface tension than water. 2. Surface tension decreases as the temperature increases. 3. As the density of the solution increases surface tension increases.

From the above the following conclusions regarding deflocculation appear:—

1. It has been shown that solutions of organic compounds cause deflocculation. It is needless to go into further discussion of this point, for the facts that have been stated are well understood by practical potters and agricultural chemists.

2. Increased temperature assists in producing deflocculation. Potters who use hot water in their blungers and brick manufacturers who use hot water in their pugmills have learned that clays slake and develop plasticity more easily with hot than with cold water. These cases find their parallel in the laboratory when clay slip is boiled in the process of soluble salt determination. Deflocculation is increased by the use of hot water.

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[1]A. C. S., Vol. VI, p. 44.

[2]Bull. 4, Weather Bureau, Dept. of Agr. p. 17.

3. Increased density[1] of a deflocculating solution does not increase its efficiency. "Ammonia[2] has a very marked action in breaking up soils containing particles less than 0.00[illegible] mm. in diameter. . . . One drop of ammonia (added to 5 grams or sample in 50 cc. of water) does not seem sufficient to break up the flocculation completely, but no great change is produced by the addition of more than 5 drops to 50 cc. of water".

The preceding facts given by our foremost agronomists, when considered in the light of the fact that increased concentration of a solution increases its surface tension, are proof of the deduction that when the potential of the solid particles is greater than that of the surrounding fluid, deflocculation ensues. In the case of the ammonia solution, increased concentration by the addition of more than 5 drops of ammonia would so increase the surface tension and consequently the potentiality of the solution as to equalize the potentials of the soil particles and the solution.

The nature of solids affects flocculation in several ways. First, if the clay or soil under examination contains a large quantity of calcium or magnesium carbonate[3], it has been found that solutions having a surface tension as low as that of ammonia will cause flocculation. Data are not available concerning clay mixtures high in other minerals, but as is about to be shown, clays that have comparatively low content of clay substance probably have as an average for the several mineral grains a low potential in comparison with the potential of water. Clays high in product of decomposition of organic matter may be flocculated by ammonia. In fact the "potential" of the

[1]Since the above was written, Von Diplom-Ingenieur Martin Böttcher, in a series of articles published in *Sprechsaal*, 1909, has shown that the deflocculation effects of various salts pass through max. points in strength of solution. Flocculation may result from the use of the same salt which at a certain strength (of solution) will cause deflocculation and vice versa.

[2]Bull. 24, Bureau of Soil, Agr. Dept., p. 24.

[3]U. S. Dept. of Agr., Bureau of Soils, Bull. 24, p. 24.

impure clays may be so low as to permit ammonia solutions to flocculate their grains.

Near[1] the surface of any soil particle there is a concentration of solutions. This is adsorption. If[2] the solid is exceedingly porous, this tendency to concentration near the surface is heightened. It is well known that salts, which are concentrated near the surface of solids are precipitated or at least are left clinging to the solids when the water is withdrawn. Soils[3], even sand, possess the property of attracting and fully absorbing salts which cannot be wholly washed out by new quantities of water. Solutions of many of the salts are materially weakened when brought in contact with clay, because of the adsorption of the salts, but if the surface of the clay particles be relatively small no weakening of the solution may be perceptible.

Summary: — The well-known facts concerning a plastic clay when wetted with water are, first, that its finer portions are composed of a countless number of minute grains, the composition of which has been shown to agree closely with that of pure clay substance; second, that even the coarser grains are composed largely of kaolinite and other minerals cemented into clusters or bundles; third, that clays having a high content of minerals other than kaolin, are flocculated by solutions having a surface tension lower than that of water, while the clays which are practically pure kaolinite in composition require for their flocculation solutions that have a surface tension higher than water; fourth, that clay particles extract salts from solutions and hold them near and on their surface at a high degree of concentration; fifth, that clay substance exhibits this property of adsorbing salts to a much higher degree than any of the common an-

[1] See Bull. 24, p. 24, Bureau of Soils.
[2] U. S. Dept. Agr. Rept. No. 64, p. 142.
[3] Compare Johnson. "How Crops Feed," p. 173.

hydrous minerals, a fact that makes the extreme fineness of the "clay substance in clays" of considerable significance.

The known facts concerning solutions are: — first, that all solutions have a surface tension which is increased with increased concentration; second, that those solutions which have a surface tension higher than that of pure water, tend to cause flocculation of kaolin grains.

On putting together the known facts concerning clay and water, it is evident that the film of water surrounding the grains of clay, (when the mass is in a plastic condition) has a very high potential, owing to the high degree of concentration of the salts that are held to the kaolin grains by adsorption; that this high potentiality manifests itself in high surface tension of the enveloping medium drawing the grains of clay together.

SUPPOSED HISTORY OF THE DEVELOPMENT OF PLASTICITY OF CLAYS IN NATURE.

Daubree[1], Cushman[2] and Mellor[3] have disintegrated feldspar in water either by grinding or by boiling. In all cases, the liquid in which the feldspar was ground contained alkali in solution. Mellor found that not only did the solution give alkaline reactions, but the "outlines (of the solid particles) could be more readily stained with saffranine or with malachite green than before the action".

Since the larger part of the clay substance is derived from the disintegration of feldspar, it can be considered that there was formed at the time of "kaolinization" insoluble hydrous silicate of alumina, soluble potash salt and soluble silicic acid. If feldspar has been disintegrated by atmospheric agencies, water and carbonic acid, and the residual mass so situated as not to allow the soluble salts to be washed away, they will be retained in

[1]An. Rep. Smithsonian Inst., 1862, p. 228.
[2]U. S. Dept. Agr., Bull. No. 92.
[3]Eng. Cer. Soc., Vol. V, pt. I, p. 72.

part by adsorption and in part by recombination, forming zeolitic masses. Data are not available to warrant the statement that plastic kaolins formed in situ owe their plasticity to these adsorbed salts, or that they even contain adsorbed salts. We do know, however, that nearly all kaolins contain alkalies[1] that can not be shown to be present as constituents of such minerals as feldspar or mica. Further we know that "the less free alkali a clay contains the more will it adsorb". We know also that clays which have been formed from feldspar under the disintegrating influence of fluorine[2] are not plastic, and contain fluorspar and and other fluorine compounds.

Cushman reports that the residue left after disintegrating the feldspar and washing out the portions which have been rendered soluble, is composed of very minute particles. If this insoluble portion, kaolin, had been formed by nature, in whose laboratory reactions, precipitations, etc., extend over an almost indefinitely longer time than is given to similar physical-chemical phenomena in the laboratory, there is no doubt but that these minute particles of kaolin would arrange themselves in the thin plate-like clusters that are characteristic of this substance, just as did the Leasburg clay cited by Wheeler. Conditions will control the size of the plate-like crystals so developed. In many kaolins these plate forms are discernible, ranging from those of sub-microscopic dimensions up to those that can be readily measured in the microscope. In a clay examined by the writer not only were there crystals of measurable size, but they appeared to be compounded, i. e., made up of several crystals, which could not be separated to an appreciable extent by vigorous shaking in distilled water. Under natural conditions, therefore, where the disintegrating water readily runs or seeps away, carrying the soluble portions and leav-

[1] C. F. Binns, A. C. S., Vol. VIII, p. 206.
[2] Jackson and Richardson, Eng. Cer. Soc., Vol. II, p. 59 (1903-4).

ing the insoluble "residual clay" in situ, we can expect to find a deposit that is more or less crystalline, depending upon the attending conditions.

These deposits, we know, are practically non-plastic. We know further from Acheson's experiments and the testimony of many agricultural chemists, that these grains can be deflocculated by organic solutions. Since surface waters generally contain organic substances in solution, and since proximity of vegetable growth can give rise to a deposit of decaying vegetable matter on kaolin beds, it is easy to see how such a deflocculation can take place in situ, and especially so if the clay be moved by running water and deposited in the lower lands. By virtue of this deflocculation, the clay has a smoother feel, i. e., texture, and thereby assumes a pseudo-plasticity. This fact has given rise to the fineness of grain theory of plasticity.

These deflocculated particles of kaolin have, as has been stated, a high adsorptive power. Whatever salts may be in solution in the passing waters, or may be carried upward from lower strata by rising waters, will be adsorbed by the kaolin particles. Now, depending upon the degree of deflocculation (hence exposure of more surface) amount of adsorption, and the kind of salt so adsorbed, plasticity will be developed.

When non-plastic kaolins are wetted with water, they are compressed into shapes only with difficulty, and when dried they either fall to pieces, as would so much fine sand, or have so weak a bond that they are easily crumbled. The finer the particles, as with the case of sand, the more readily can they be shaped into pieces that will retain their form, but no matter how finely sub-divided the grains may be, the mass is still very friable. In this fine condition the kaolin no doubt possesses every chemical and physical property possessed by the plastic kaolin (ball clay) save that of plasticity. It has water chemically combined, molecular attraction, and adsorbing properties. It becomes plastic only when it has adsorbed salts, the solution of which exhibits a high surface tension, or as

Whitney would express it, which have a relatively high potentiality. Clays having adsorbed salts, and consequently plasticity, are no longer friable when molded but, on the contrary, are exceedingly hard.

It is because of this adsorption property which in kaolin grains seems to be manifested to a higher degree than in any other mineral substance, with perhaps the exception of zeolites, that many find reason to believe that plasticity is due to a pectoidal structure of the kaolin grains. Since, however, they cannot show that those substances which are known to have a pectoidal or colloidal structure can be made to show or develop plasticity, and since colloids cannot be extracted from plastic clays, rendering them non-plastic, nor added to non-plastic kaolins rendering them plastic, we must conclude that this theory is hardly tenable.

To what this adsorptive power of inorganic compounds[1] is due has not yet been determined. We, however, must accept the existence of this property as a proved fact. It should be considered as a physical property just as much so as color, hardness, etc. Most if not all mineral substances have this adsorptive property in some degree. Quartz has a measurable degree of adsorptive property. In fact botanists, because of its peculiarly limited degree of adsorption, use quartz on which to germinate seeds. We must also concede that when water is added to a clay, that portion which envelopes the very minute solid particles, which have relatively large surface area in proportion to their volume, and holds salts by adsorption, will be highly concentrated (most likely super saturated): that the potential of this film will be very much more than those portions of the water farthest away from the solid particles; and finally, as shown by the flocculation of the clay particles, that the potential of this saturated film of water is higher than the potential of the kaolin particles.

[1]Mineral substances other than kaolin are known to possess adsorptive properties. Carborundum (artificial) possesses a notable adsorptive power.

The writer bases his assumptions as to the cause of plasticity on known facts: — Adsorption of salts by the kaolin grains and the consequent high potential of the water film which surrounds the grains when a clay mass is in a plastic condition. On these assumptions, the cause of the latent plasticity when clay is dry and the developed plasticity when it is wet, are obvious.

Fineness of grain, molecular attraction, adsorptive property, are conditions that permit of the adsorption, or at least the retention near the surface, of salts. In other words, they are necessary conditions, just as the addition of water to fill the pores and furnish the enveloping saturated solution about the grains is a necessary condition.

Comparatively high viscosity, due to super-saturation plus high surface tension, results in the slippery medium which reduces friction between the grains and permits flowage under pressure without rupture.

To claim that the clay particles must be wrapped about by a colloidal coating because the clay responds in like manner in one test with colloids is of the same order in logic as claiming the existence of an element "phlogiston" which all chemists did prior to the discovery of oxygen by Lavoisier in 1774. The one test in which clays and colloids behave alike is adsorption of salts. It is necessary to show an agreement in more than one property, however, before two specimens can be said to be of the same or even similar kind. This has not been done in case of clays and colloids.

PARALLELISM BETWEEN ADSORPTION AND COLLOIDAL THEORIES.

Both theories were initiated by and built up on the adsorption of salts. The ability of clay grains to hold salts so strongly that they can not be easily removed[1]

[1] Because of the extreme difficulty encountered in leaching soluble salts out of clay we have as yet no data from which a relation between observed plasticity and reported amounts of soluble salts can be traced. In the usual "soluble salt" determination only a portion of the salts is extracted. No one has gone "to the limit" in soluble salt extraction.

by solution in water is a manifestation of this adsorption property.

In the colloid theory it is maintained that these salts are held as reversible "gels". That when wetted with water they hydrolize or go partly into solution forming a jell-like or colloidal film about the grains. When once adsorbed by clay common salts are no longer such, but are transformed into "gels" or colloidal materials. The philosophy of this change is not of concern. With like complacency, if needs be, the metal would lose phlogiston because on heating it appeared to lose something and regain this phlogiston by reduction because it appears to gain something.

Instead of the formation of a colloid, the adsorbed salt theory is content with considering adsorption as a property in the same sense as hardness or fusibility, etc. It is content with the plain and well established fact that all kinds of matter has a given attraction for other matters of opposite charge, which in many cases has been measured. This is often called molecular attraction. The adsorbed salt theory recognizes that, depending upon the substance with which it is in contact, water surfaces may show surface tension or surface pressure. It is content with the fact that solution of different salts have different surface tension, and that the higher the surface tension, the more strong is the pull of the surface particles toward the center of the water mass. With increased concentration of salt in solution, we have increased surface tension. With a grain of clay substance coated with a salt or salts surrounded by a water film, the surface tension of which is increased by molecular attraction between the water particles and the clay grain as well as by the salt which it has taken into solution, to the point of super-saturation, it is stepping but a little ways beyond observed and measured facts and conditions to credit a high degree of viscosity to this film which results in true plasticity of the mass.

The point of similarity in the conception of this film is that it is highly saturated, in fact approaching in one sense a viscous solid condition. In the colloid assumption this salt solution, owing to some property of the clay (some say pectoidal structure), becomes so concentrated that it is no longer an ordinary solution but a colloidal solution. In the adsorbed salt theory it is a common solution still, altho concentrated to an unusual degree because of the adsorptive property of clay.

It is very difficult to see why clay should be so different from other mineral substance that it has the property of transforming common solution into colloidal solution that results in true plasticity or that the grains are coated with colloids which dissolve and dissociate salts. Why do not other substances have this same property?

The two theories agree in that solutions of strong electrolytes cause flocculation and of weak or non-electrolytes deflocculation. The colloid theorists claim that the electrolytes ionize, that ions neutralize the static charge of the colloid resulting in flocculation.

Thoroly believing in the ionic theory and in the carrying of opposite charges by the acid and basic ions, we believe also in the established facts that (1) but little of the salts are ionized in any solution; (2) that these same ionized salt solutions coincidently have a high surface tension, a phenomenon as remarkable, as difficult to explain, but less mooted. Ionization may result in surface tension. What the philosophy of this coincidence in ionization and surface tension may be need not enter into these discussions. The fact that these salts do give high surface tension, however, must be recognized.

Plasticity is the result of purely physical conditions and properties, — adsorption, solution, molecular attraction and high surface tension. Going beyond the consideration of these physical properties and saying that they combine in the transformation of ordinary salt solutions into colloidal solutions or are the effects with colloids as the cause is taking a step into a region of pure

supposition that is entirely uncalled for. If we accept Mr. Ashley's definition of a colloid—"A colloid may be defined as almost any matter that is not crystalline or crystaloid"—then very likely a considerable portion of our clays is colloidal. But why this resort to a broad definition?

Mr. Ashley: Mr. President, the weak point in Mr. Purdy's theory, as I see it, is that it would apply, for example, as well to flint as to clay. If you mix salts with flint why doesn't it become plastic? It has a surface factor of about 125 and there are quite a number of clays with a surface factor of 125. Texas Kaolin is 123 and there is one in my list with only one hundred. Under the adsorbed salts theory, any flint should be as plastic as a clay if it has the same amount of salts put with it, but I believe no one has obtained that.

If Mr. Purdy thinks there is some peculiar attraction for water, I think so, too; and call that peculiarity colloidal matter. In a legal case involving poison, the chemist must isolate the poison. Mr. Schloessing isolated the "poison" and ever since, to some extent, chemists have been isolating colloidal residues.

I had hoped in view of the number of practical men here acquainted with most of the clays named on the chart, that they would state their opinion as to the plasticity of these clays, or state wherein this chart deviates from their experience.

Mr. Purdy: I distinctly stated that "clay" particles have an adsorptive power far in excess of that of any other mineral substance. It is as peculiar to clay grains as hardness is to the diamond. Where there is no adsorptive power of sufficient strength to hold the quantity of salts necessary you can not expect plasticity. If Mr. Ashley's reasoning regarding colloids is correct let me ask why can we not add colloids to flint and obtain plastic masses? I refer here of course to true plasticity—not pseudo-plasticity as we have in magnesite bricks, which,

in order to facilitate moulding, are compounded from normally burned MgO (the plastic medium), and over-burned MgO.

We have isolated the poison (soluble salts) on frequent occasions. On the inability to isolate what Mr. Ashley considers the poison (colloids) we have a serious stumbling block to the theory he advances.

Referring to the rating of clays by Mr. Ashley by means of his colloid modulus, let it be admitted that he has succeeded in placing the clays in proper sequence according to their comparative plasticity. In the formula, however, he has surface factor as the denominator. Now the finer the clay, the larger will be its surface factor and hence the finer the clay, the smaller its colloid modulus. This would mean that the finer the clay, the less plastic it would be. Now practical experience certainly proves that quite the reverse of this is true. It must be, therefore, that no matter how true to facts in the case the colloidal theory may be, Mr. Ashley's modulus is built up on assumptions that are contrary to facts. His success in placing the clays he cited in proper sequence according to their plasticity must be quite accidental. It is surprising that he did not find more exceptions to his rule. At least, he can not properly use his final data (which involve incorrect assumptions as to influence of size of grain) as evidence in support of the colloidal theory of plasticity.

I did not expect to be understood as denying the existence of colloidal matter in clays. If colloids exist at all, clays will surely contain some.

If the theory concerning hydrolysis of compounds of weak bases and weak acids is true, then Al_2O_3 2 SiO_2 2 H_2O would on treatment with water be hydrolysed[1] to some extent resulting in colloidal alumina and colloidal silica. Theoretical reasoning also indicates that these two weak components would not ionize and thus retard or prevent completion of the hydrolysis of the Al_2O_3 $2SiO_2$ $2H_2O$, con-

[1]Suggested to the writer by Wilber Stout.

verting kaolinite entirely into two colloidal components. Just how far facts bear out this theoretical reasoning I do not know. I do know however, that most clays contain but a trace of silica that can be identified as soluble by the customary analytical methods. When it comes down to actual and unmistakable proof we would find it a very serious proposition to establish beyond doubt the presence of kaolinite in the vast majority of clays.

We could thus continue exposing the inadequacies of our means of observations and analyses, and the apparent discrepancies between theory and facts. For instance, if we carry our conceptions of the possible degree of subdivision of solid matter to approximate infinity then any solid matter may be conceived as having the possibility of existing in a semi-liquid (colloidal) state even at ordinary temperatures (25° C.). This is what is done when the finest portion of a clay is considered as being in a colloidal condition. Now while I can not believe that clays are devoid of colloidal matter, I can not believe with Mr. Ashley that all of these finest particles of the clay material are in a colloidal condition and hence responsible for the plasticity of the clay. I hope some one will examine clays through an ultra violet microscope or a dark field microscope. An ordinary microscope will not magnify these small grains so as to permit of a description of their properties, while these more highly magnifying microscopes may possibly do so. If with these, the finest grains are still too small to be seen, then we must be content with the colloid postulations.

Mr. Ashley: In preparing the paper on the Colloid Matter of Clay, the writer examined the mass of evidence for the various views, and selected those that in his judgment are most entitled to full acceptance. In each case, he attempted to give credit to the first writer on each phase of the subject. Thus Schloessing was credited with isolating the colloidal matter of kaolin in 1874; but the writer did not mention that ever since then, it has been

the practice of many agricultural chemists to report in their soil analyses as colloidal all that matter remaining in suspension 24 hours in slightly ammoniacal water.*

Every physical chemist and agricultural chemist knows that the finest constituent of soils is not granular, but jelly-like. Indeed, it is difficult with the highest powers of the microscope to find any crystalline matter at all in the most plastic clays. As all competent authorities have agreed in naming this non-crystalline, jelly-like constituent "colloid", the writer could only accept the best usage, and describe the many colloid properties, including adsorption.

As the finest matter of clay is not granular, any calculations based on the "grains" of the "finest" matter are absurd. The assumption of an average diameter of 0.0005 mm. for these imaginary grains is wholly unwarranted. Any theory that ignores the non-crystalline, jelly-like matter that is actually present in clays is unjustified. It is the colloid matter in the spaces between the grains that supplies the peculiar property of clay grains that makes it possible "to furnish each grain its water envelope by which and in which conditions are rendered favorable for the development of plasticity."

As the colloid matter of clay possesses far greater internal or cellular surfaces than can be attributed to the finest grains, surface tension should have much greater effect on clays than on almost wholly crystalline substances practically without colloids, such as ground quartz. The writer has presented evidence that soluble salts have great effect upon colloids, including clay colloids. But they have very little effect on the crystalline grains of kaolin.

The writer cannot agree with the method of recalculating analyses used in regard to Tables II and III of the preceding discussion. Taking the finest grade: a method

*H. W. Wiley, Principles of Agricultural Analysis I., 200-202, 231 (1894).

that accounts for only 0.88 kaolin, 0.12 feldspar, and 0.18 quartz, and that ignores 0.18 Fe_2O_3 0.05 FeO, 0.12 MgO, 0.05 CaO, 0.04 TiO_2, and 0.42 loss on ignition (taken as H_2O) is too incomplete to be satisfactory. Analyses of crystal samples of kaolinite and feldspar show these ingredients. Why, then, are they excluded from the rational classification?

The writer cannot see the profit of such extended discussion until the nature of the soluble salts is more accurately ascertained. After a portion have done duty as "constituents of the cementing salts" for the coarsest grains, the entire amount is taken to "account for nearly all of the alkali in the finest grade". That all should be with the finest matter and a portion also with the coarsest matter is an amusing piece of logic.

In the summary of the preceding discussion, various positive assertions require attention.

Contrary to that summary, plasticity and certain amounts of colloid gels always go together.

Contrary to that summary, a German patent has just been issued for destroying the plasticity of kaolin by extracting the colloids by alkali, and another for improving the plasticity of clays by first dissolving the colloids by alkali, adding other colloids, and then reforming the gel by acids. Acheson's patent was for the improvement of plasticity by the addition of substances that are generally recognized as colloids.

Contrary to that summary, high viscosity is the measure of high internal friction in a fluid, not a means of eliminating friction.

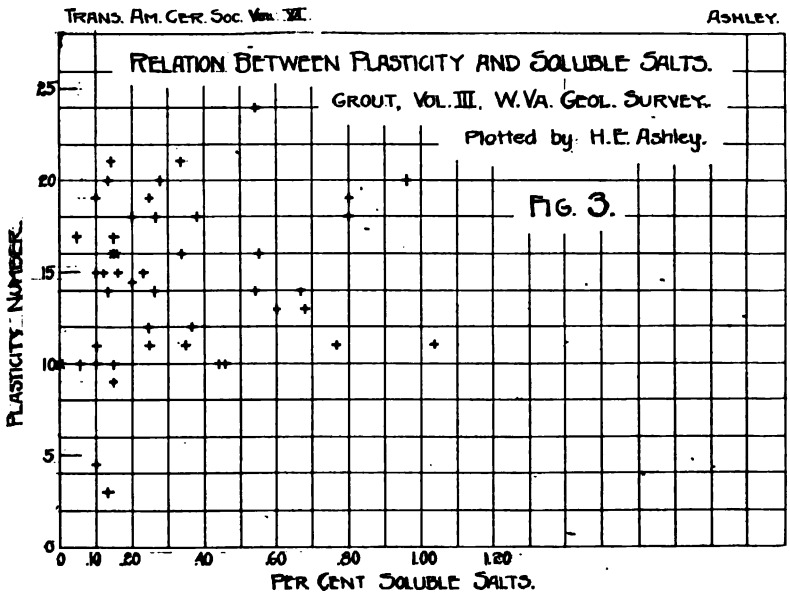
Contrary to that summary, in all its properties, the jelly-like constituent of clays behaves like other colloids.

Not "content with considering adsorption as a property in the same sense as hardness or fusibility, etc.," physicists consider it as an effect of surface tension.

Contrary to that summary, colloidal solution is the destroyer of plasticity.

Contrary to that summary the writer asserts that the specific nature of each ion determines whether or not it will stabilize or deflocculate a gel; and further that alkaline monovalent basic ions will deflocculate clays under favorable conditions and most polyvalent and complex basic ions will coagulate clay sols.

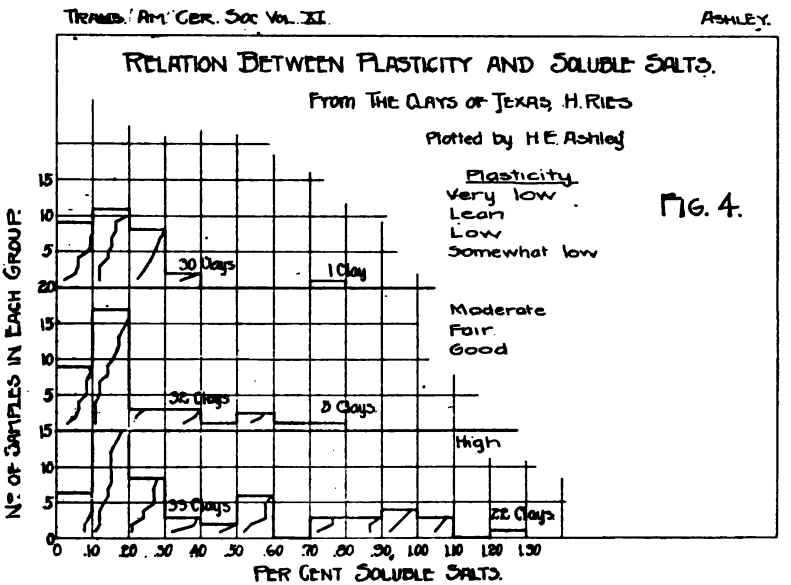
Two recent investigators have given in their reports estimates both of the soluble salts present in clays and of the plasticity of the same clays.



Grout* estimated plasticity as the product of a deformation by a force producing a deformation. He said that his plasticity numbers so derived in no case put a clay of low plasticity above one of higher. Each of his observations is plotted in Fig. 3. Absolutely no relation is shown between the plasticity and the percentage of soluble salts present.

*West Virginia Geological Survey, Vol. III., (1905).

Ries* estimated plasticity by feel. In Fig. 4, his results have been arranged by the writer in 3 divisions, low, moderate to good, and high plasticity. With from 0 to 0.10 per cent soluble salts, 9 clays showed low plasticity, 9 moderate to good, and 7 high plasticity. With from 0 to 0.40 per cent soluble salts, 30 clays showed low plasticity, 32 clays moderate to good plasticity, and 33 clays high plasticity. Consequently if a clay shows less than 0.40



per cent soluble salts, this measurement gives no idea whatever as to the plasticity of the clay. With over 0.40 per cent soluble salts 1 clay had low plasticity, 5 moderate to good, and 22 high plasticity. Hence a high percentage of soluble salts, as Seger pointed out, is *likely* to be associated with high plasticity.

In the preceding discussion Mr. Purdy has mistaken an effect for the cause, and has denied the cause.

*The Clays of Texas. Bull. of the University of Texas, No. 102 (1908).

NOTE ON THE VISCOSITY OF CLAY SLIPS.

BY

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It is evident that there exists a relation between the plasticity of clays and the viscosity of slips made from them by the addition of water. The senior writer has suggested the determination of the viscosity of slips in the examination of clays as to their relative plasticity (*Trans. Am. Ceram. Soc., Vol. X*) by means of a viscosimeter of the Coulomb type. In this note an attempt has been made to simplify the method for the use of the practical man, especially by eliminating the more complicated computation. For this purpose the Stormer viscosimeter[b] was adopted, an apparatus designed for the determination of the viscosity of lubricating oils.

This instrument consists in brief of a vertical shaft to which paddles are attached and which is driven by means of simple gearing from a grooved pulley. Motion is imparted to the latter by means of a weight attached to the pulley by a cord. The weight used in these experiments was 200 grams. To the paddle shaft a revolution counter is attached. The method of operating the instrument is very simple. If, for instance, it is desired to determine the viscosity of a fluid, the latter is poured into the square receptacle, taking care that the same level is maintained for each test. The cup is then raised so that the paddles are immersed, and by releasing a brake the weight is caused to descend, thus revolving the pulley and transmitting motion to the paddle shaft. By means of

a. By permission of the Director, U. S. Geological Survey.

b. Brought on the market by the Bausch and Lomb Optical Co., Rochester, New York.

a stop watch indicating 1/5 seconds the time required for the paddles to make 100 revolutions is determined. It is also necessary to determine the time taken for the same number of revolutions in air, thus taking into account the friction of the instrument.

For the purpose of illustration, let us assume that 100 revolutions of the paddle in air require 2 seconds, in water 10, and in a certain clay slip, 14 seconds. The relative viscosity of the slip as expressed by this instrument is then obtained by deducting 2 seconds from the time required in water and in the slip which gives us 8 and 12

seconds respectively. The viscosity of the clay slip in terms of water, which should be at the same temperature, then becomes 12÷8=1.5.

It is evident from a study of the apparatus that it makes no claim to scientific accuracy since the air friction has been neglected, as well as the force expended upon the whirling of the liquid by the centrifugal action, amount of slip, etc. It is, therefore, not to be considered in connection with the determination of the absolute viscosities by instruments of the Coulomb type, as discussed by Clerk Maxwell[a], Meyer[b] and Stokes[c]. What has been said about the technical viscosity determination in the work of Colcan[d], Doolittle[e] and Engler[f], namely, that all of these determinations furnish constants of no value from the absolute standpoint unless the method is given in each case, applies still more strongly with the Stormer instrument.

This would be a serious handicap for the study of the viscosities of clay slips were it not for the fact that absolute values are not necessary, since in our work we seek simply to correlate and arrange our clays in the order of their plasticity. Thus while it is immaterial to us to know the absolute viscosity of a certain clay slip we do appreciate knowing that clay *x* is twice or 1 1/2 times as plastic as clay *y*. At the same time, by making up a series of slips and plotting curves representing the viscosities of a clay blended with different amounts of water we obtain relations which are exceedingly characteristic for each type of clay. This knowledge we can obtain with practically any instrument not handicapped by serious mechanical defects.

Again, since we are dealing not with solutions, but with suspensions of high viscosity, and since the materials

a. Phil. Trans. (1866) 156, 249-268.
b. Pogg. Ann. (1865) 125, 177.
c. Camb. Phil. Soc. Trans. (1850) p. 9, II, 8.
d. Journ. Soc. Chem. Ind. (1886), p. 359.
e. Jour. Am. Chem. Soc. (1893), 15, 173, 454.
f. Jour. Soc. Chem. Ind. (1893), p. 292.

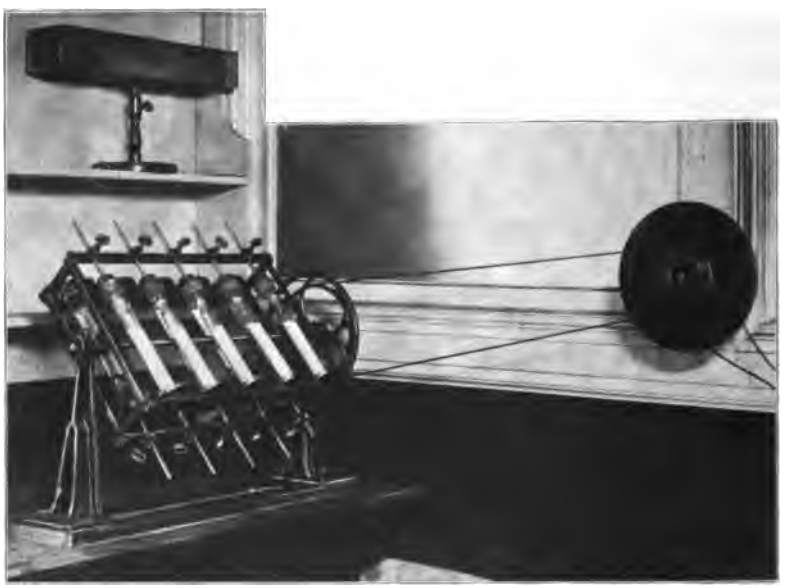
to be tested have a decided tendency to settle, the futility of desiring to obtain absolute values is apparent. The exact work that has been done upon the viscosity of fluids has failed to deal adequately with solutions of high viscosity and we have practically no knowledge as to the internal and external friction of suspensions from the theoretical standpoint.

The Stormer viscosimeter is capable of further mechanical improvement, such as the substitution of a suitable screw for the paddles to reduce the vortex action. The mechanical construction might likewise be improved somewhat with respect to accuracy of fitting and greater elimination of friction.

In the work with clays the decided advantages possessed by this instrument are, first, the thorough stirring which the slip undergoes during the determination, thus preventing all settling and doing away with a grave error in operating with the coarser clays; second, the possibility of working with heavier slips and higher viscosities; third, the simplicity and rapidity of operation and calculation. For these reasons the writers believe that this type of apparatus may become a useful tool in the hands of the practical man for comparing the plasticities of his clays.

The preparation of the clays for the test consists in simply weighing out a certain quantity of the material, after making a determination of the moisture factor, say 100 grams, and of a sufficient amount of water and shaking thoroughly, so that the slip becomes as thick as possible and yet permits the paddle to revolve. The constant of the apparatus for distilled water is then found by filling the cup to the desired height with water and taking the time of 100 revolutions. The same thing is done for rotation in air. Several check readings should invariably be made in each case. It is important that the temperatures of the water and the slip be the same and this point should be watched closely. Likewise, it is necessary to make frequent determinations of the water and air constants which are liable to fluctuate.

For the determination of the viscosity of more dilute slips more water is added, the amount of which is easily calculated from the known and desired strength of the slip. If, for instance, we have 100 grams of slip containing 50 grams of clay, and we desire to make one containing 40% of solid matter, the weight of the water to be added is obtained from the relation $100 \times 50 = x \times 40$, where the value of x is found to be 125 grams. Subtracting 100 from 125 we find 25 grams of water to be the amount



necessary. In this way five or six dilutions are made and their viscosity determined so that a curve may be plotted which is characteristic of the clay.

As regards the blending of the clay with the water the method practised in this work is to place the weighed amounts of water and clay into a wide-mouth bottle with a ground-glass stopper and fastening the receptacle in the shaking machine illustrated in the accompanying half-

tone. The apparatus makes 15 revolutions per minute and the shaking is continued for 10 hours. A little shot is placed in the bottle to facilitate the breaking up of the clay particles. The slip is then shaken through a 20-mesh sieve and poured into the viscosimeter cup.

It is evident that if the clays are ground instead of being shaken the slip will reach a higher viscosity due to the breaking up of more inert clay particles, and thus the effect of grinding may be followed quite accurately. Similarly, the effect of additions of sodium carbonate or sodium silicate to casting slips may be readily demonstrated.

In this work ten clays were examined which represent a variety of materials of various degrees of plasticity. The same clays are being studied in another investigation with regard to their behavior after having been subjected to a preliminary drying treatment at various temperatures. They are as follows:

1. English china clay, J. Poole No. 1, considered the highest grade of the English kaolins, but not commonly imported.

2. An extremely fine glacial clay from Albert Lea, Minn., troublesome to dry and of considerable plasticity. About 93.5% passes the third can of the elutriating apparatus.

3. Prall sagger clay, Woodbridge, N. J., a decidedly plastic material of excellent bonding power, but of safe drying behavior. Coarser grains mostly quartz; about 82% passes the third can.

4. Texas kaolin, "Lone Star" brand, from Edwards Co., Texas. A fireclay consisting of clay grains which are not broken down by the shaking treatment and extremely fine clay matter. Grinding increases the plasticity of this clay immensely and in this way it is capable of great improvement by the reduction of the comparatively coarse clay grains. About 49% passes the third can.

5. Tennessee ball clay No. 3. A clay of great bonding power, somewhat finer as a whole than the Prall sagger clay. 82.2% passes the third can.

6. St. Louis fireclay, Highland Fire Clay Co., St. Louis, Mo. A high grade fireclay, but lacking in plasticity owing to insufficient reduction of clay grains. Grinding at once improves the plastic quality simply by disintegrating the coarser, wax-like clay particles. 38.8% passed the third can.

7. Peoria joint clay, from the yard of A. E. Giles, Peoria, Illinois; a typical fine-grained glacial clay, giving trouble in drying. 49.8% passed the third can.

8. An exceedingly plastic clay from Ft. Pierre, North Dakota, through the kindness of Prof. Orton. Impossible to dry without cracking, owing to extreme fineness. 91.9% passed the third can.

9. Albany slip clay, procured on the open market. A plastic glacial material of great fineness. 84% passed the third can.

10. Joint clay, from J. W. Stipes, Urbana, Ill. A plastic glacial clay, difficult to dry, due not so much to great fineness of grain, as to "joint" structure of plastic clay base. 47.2% passed the third can.

The accompanying diagram illustrates the results of the viscosity determinations and it will be observed that there are certain irregularities in the curves which evidently are due to the apparatus and probably to the design of the paddles. Somewhat smoother curves were obtained by working with a lighter weight, 150 grams, but the highest viscosity attainable with this load was too low for the purpose of the experiments. With the smaller weight the existence of negative viscosities was shown for the low percentages of some clays which were not indicated with the heavier weight.

If now we study the arrangement of the curves by following a constant viscosity line, say, the viscosity value of 2 from left to right, we observe at once that the clay showing the above viscosity with the smallest amount of

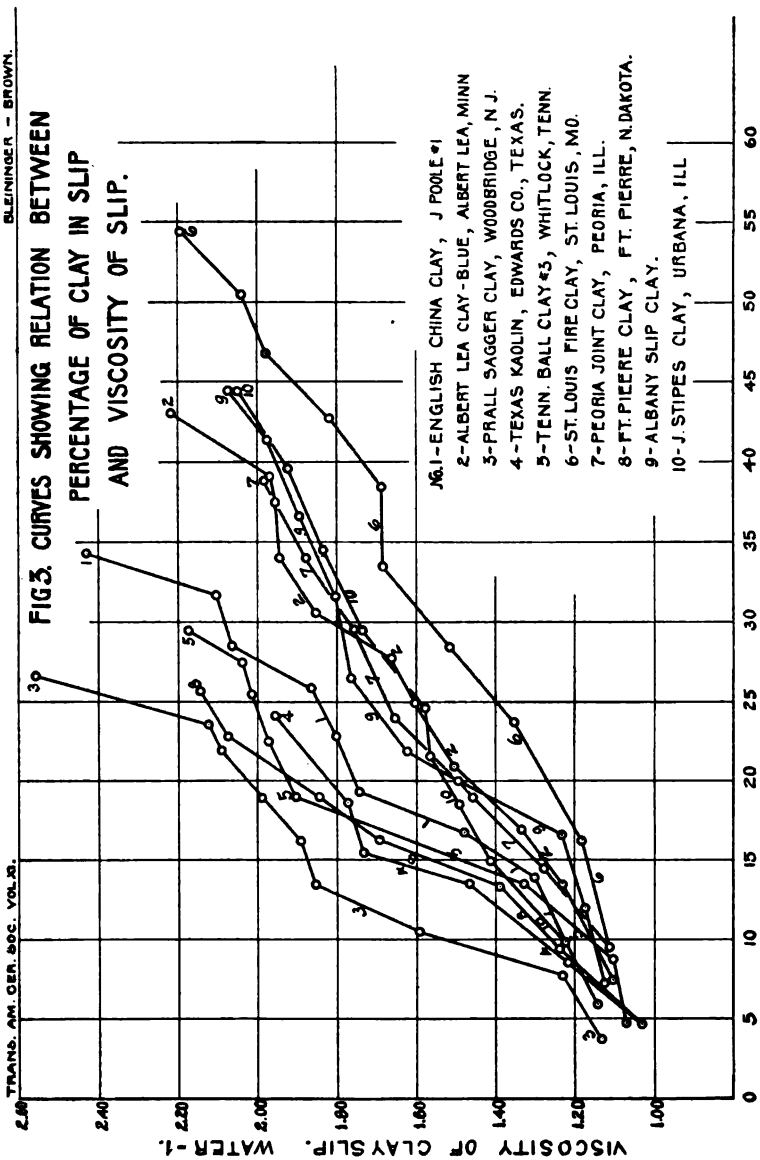

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FIG. 3. CURVES SHOWING RELATION BETWEEN PERCENTAGE OF CLAY IN SLIP AND VISCOSITY OF SLIP.
NO. 1 - ENGLISH CHINA CLAY, J POOLE #1
2 - ALBERT LEA CLAY - BLUE, ALBERT LEA, MINN
3 - PRALL SAGGER CLAY, WOODBRIDGE, N J.
4 - TEXAS KAOLIN, EDWARDS CO., TEXAS.
5 - TENN. BALL CLAY #5, WHITLOCK, TENN.
6 - ST. LOUIS FIRE CLAY, ST. LOUIS, MO.
7 - PEORIA JOINT CLAY, PEORIA, ILL.
8 - FT. PIERRE CLAY, FT. PIERRE, N. DAKOTA.
9 - ALBANY SLIP CLAY.
10 - J. STIPES CLAY, URBANA, ILL
VISCOSITY OF CLAY SLIP. WATER - 1.
% CLAY (BY WT.) IN SLIP.
2.60
2.40
2.20
2.00
1.80
1.60
1.40
1.20
1.00
0
5
10
15
20
25
30
35
40
45
50
55
60

material is evidently the most viscous substance and, if viscosity is an indication of plasticity, the most plastic one. The first group comprises five clays of which the Prall sagger clay is the most viscous one with the English china clay as the lowest member. Referring to the percentages along the abscissa a viscosity of 2 is equivalent to 19.5% of the sagger clay and to 27.5% of the English kaolin. The latter then should be 0.71 as plastic as the Prall clay if the above assumption holds. The Ft. Pierre surface clay is brought into this group by its abnormal plasticity, which is uncommon for an impure material of this kind. Although the Minnesota clay is as fine, its plasticity is not high enough to bring it into this group.

In the second group we find all of the four glacial clays collected in a remarkable manner, which might be taken to indicate that the plastic clay base is of the same character in all of them and that the non-plastic dilution must be about the same as regards the surface factor.

In the third group we have the St. Louis fireclay which is the only representative of this class of materials.

The conclusion to be reached is that the viscosity of clay slips is a function of plasticity. This, however, requires further analysis and there is reason to believe that by correlating this constant with the surface factor of the non-plastic constituents separated out by elutriation, the drying shrinkage and the water required in the plastic state, a numerical value should be obtained which represents the true plasticity with a considerable degree of accuracy. Likewise, the ease with which a clay dries would be given by a similar expression. The correlation of these factors is reserved for further work.

A CHEAP ENAMEL FOR STONEWARE.

PART II.

R. T. STULL, Urbana, Illinois.

The last contribution of "A Cheap Enamel for Stoneware," in Vol. X, was sent in for publication three days after the last trials came from the kiln. The most promising enamels of the work done up to that time were the members of Series IX, and the best one of the series was No. 35.

As has been noted, no craze marks were observed on No. 35, when taken from the kiln. After three weeks' time a craze mark appeared on the bottom of one trial. Crazing has been going on gradually until now the trials are completely checkered with craze marks. The author is of the opinion that the crazing is due to the softness of the body rather than to the glaze itself, since the trials were burned at cone 01.

SERIES X.

The maturing temperature of No. 35 is altogether too low for the stoneware body and too high for other types of ware, notably those maturing at cone 04. Hence it was thought advisable to construct a series starting with a glaze of the same type as No. 35, but which should be more fusible. The RO, Al_2O_3 and P_2O_5, which are the same as those in No. 35, are kept constant throughout the series, the two variable members being SiO_2 and B_2O_3.

Each succeeding member has the B_2O_3 decreased one tenth and the SiO_2 increased accordingly. Two fritts were

made for Series X, which have the following formulae and batch weights:

Fritt G.

Formula			*Batch weights*	
.8571 CaO .1429 ZnO	.357 Al_2O_3	2.3 SiO_2 .2857 P_2O_5	Bone Ash	30.75
			Zinc Oxide	4.03
			N. C. Kaolin	32.09
			Flint	33.13

Fritt H.

Formula			*Batch weights*	
.25 K_2O .75 CaO	.5625 Al_2O_3	2.125 SiO_2 .250 P_2O_5 1.250 B_2O_3	Feldspar	30.80
			Bone Ash	17.09
			N. C. Kaolin	17.83
			Boracic Acid	34.28

Fritt G was calcined in a flinted sagger at cone 8. Fritt H was fused in a flinted crucible and quenched in water. Both fritts were ground dry to a fine powder ready for weighing.

Glazes.

Formulae								*Batch weights*					
Glaze No.	K_2O	CaO	Zno	Al_2O_3	SiO_2	P_2O_5	B_2O_3	Branuywine Feldspar	Fritt G	Fritt H	Zinc Oxide	Georgia Kaolin	Flint
36	.2	.6	.2	.55	2.3	.2	1.0	.....	.....	81.90	4.45	7.07	6.58
37	"	"	"	"	2.4	"	.9	3.06	5.28	73.91	4.24	7.09	6.42
38	"	"	"	"	2.5	"	.8	6.14	10.60	65.88	4.02	7.11	6.25
39	"	"	"	"	2.6	"	.7	9.24	15.94	57.80	3.81	7.13	6.08
40	"	"	"	"	2.7	"	.6	12.35	21.31	49.68	3.59	7.15	5.92
41	"	"	"	"	2.8	"	.5	15.48	26.71	41.51	3.38	7.17	5.75
42	"	"	"	"	2.9	"	.4	18.63	32.14	33.30	3.16	7.19	5.58
43	"	"	"	"	3.0	"	.3	21.79	37.60	25.04	2.94	7.21	5.42
44	"	"	"	"	3.1	"	.2	24.79	43.09	16.74	2.72	7.23	5.25
45	"	"	"	"	3.2	"	.1	28.17	48.60	8.39	2.51	7.25	5.08
46	"	"	"	"	3.3	"	.0	31.39	54.16	.....	2.28	7.27	4.90

These glazes were applied to bone dry stoneware crocks but flaked so badly on drying that the series was abandoned. A few subsequent dips of the two extremes of this series (Nos. 36 and 46) worked very satisfactorily on biscuit. No further investigation was made into the working qualities of the members of this series on biscuit since the work is mainly along the line of single fire enamels.

SERIES XI.

Series X was modified in series XI to overcome flaking. In this series the same formulae are used as in series X, the difference being that in series XI the raw clay is increased from 0.1 to 0.15 and Tennessee ball clay No. 3 is used in place of Georgia kaolin. This required the making of two new fritts (I and J), since the excess clay above 0.1 in series X was fritted.

Fritt I.

Formula			*Batch weights*	
.5 K_2O / .5 ZnO	.5 Al_2O_3	3.0 SiO_2 / 2.5 B_2O_3	Brandywine Feldspar	44.28
			Zinc Oxide	6.44
			Boracic Acid	49.28

Combined weight 494.

Fritt J.

Formula			*Batch weights*	
1.0 CaO	.3⅓ Al_2O_3	1.3⅓ SiO_2 / .3⅓ P_2O_5	Bone Ash	45.06
			N. C. Kaolin	37.50
			Flint	17.44

The first one was drop fritted while the latter was calcined to cone 8 in a flinted sagger. Both were reduced to powder and used in this form in weighing up the glazes.

Batch Weights Series XI (Having the same successive formulae as Series X).

Glaze	Brandywine Feldspar	Fritt I	Fritt J	Zinc Oxide	Tenn. Ball Clay No. 3	Flint
47	.....	53.89	35.56	.....	10.55	.....
48	3.05	48.63	35.66	0.44	10.58	1.64
49	6.11	43.35	35.75	0.89	10.61	3.29
50	9.19	38.03	35.85	1.34	10.64	4.95
51	12.28	32.69	35.95	1.79	10.67	6.62
52	15.40	27.32	36.05	2.24	10.70	8.29
53	18.53	21.91	36.15	2.70	10.73	9.98
54	21.68	16.48	36.25	3.15	10.76	11.68
55	24.85	11.02	36.35	3.61	10.79	13.38
56	28.03	5.52	36.46	4.08	10.82	15.09
57	31.23	.....	36.56	4.54	10.85	16.82

Three burns were made of the members of this series. The first four members were burned to cone 04, the first six to cone 01, and all were burned to cone 6.

Cone 04 Burn.

No. 47 in this burn appeared to be well matured and glossy. It was not quite so opaque nor light colored as No. 35 (see p. 239 and p. 241, Vol. X, *Trans. A. C. S.*). A few small bubbles appear on the exposed rim. The glaze crazes some on the soft buff body.

No. 48 is the best glaze of the burn, though it has a very slight tendency to pull away from the rim. It is nearly as opaque and light in color as No. 35. It crazes some.

No. 49 (having the same formula as No. 35) is underfired, being a little dull in texture. It is opaque and nearly white, crazes.

No. 50 is decidedly underfired, having the appearance of highly vitrified porcelain. Badly crazed. In two places the glaze has loosened and stands out from the body.

Cone 01 Burn.

No. 47 is glossy, but the opacity has decreased, giving a translucent glaze. Bubbling has also increased, crazing decreased.

The opacity of No. 48 has also diminished. The glaze in this burn is otherwise good.

No. 49 is opaque but not quite so light colored as No. 35. A slight tendency to flake appears. The glaze shows a few craze marks.

No. 50 is more opaque than 49 though not quite so glossy. Crazes badly.

Nos. 51 and 52 are underfired and crazed.

Cone 6 Burn.

In this burn all glazes show small bubbles up to No. 55. No. 47 is bubbled the worst, having a frothlike appearance. Bubbling decreases towards No. 55. No. 55 has a pitted appearance. These glazes are undoubtedly overfired.

No. 56 is well matured and shows no bad defects. Its whiteness is a little better than that of a good bristol.

No. 57 is a little whiter than 56 though not brilliant enough to be a good glaze. It would be better at cone 7.

Conclusions on Series XI.

The glazes of this series are capable of producing glossy opaque enamels when given the right heat treatment. If a little underfired, they are dry and dull. When slightly overfired, they lose opacity and begin to develop bubbling. The range of temperature is very short, not over 1½ cones at most. For this reason they are not commercially valuable.

The writer's practical experience in glazes in which magnesite was used, brought out the fact that MgO possessed strong opacifying properties. Tin enamels containing 0.25 MgO required less tin oxide in order to produce the same degree of opacity than those containing no MgO. It was also observed in testing feldspars that soda feldspar of a pure grade fused to a whiter and more opaque bead than potash spar. The crystalline form of soda spar generally occurs as a porcelain white mineral called Albite; potash spar, or Orthoclase, on the other hand, is more translucent and dark in color.

If it is true concerning bases belonging to the same chemical group or family that those of low molecular weight possess a lower degree of solubility in a silicate fusion and a higher velocity of crystallization than bases of high molecular weight, then less molecular quantities of Na_2O and MgO would be required to produce "supersaturation" and "incipient crystallization" than the bases of their corresponding groups having higher molecular weights, namely K_2O and CaO.

Acting upon the above suggestions, series XII and XIII were constructed. It will be noted that the members of these series are glazes of the bristol type, in which Na_2O is substituted for K_2O and MgO replaces CaO. In these two series the RO is kept constant.

SERIES XII.

Formulae						*Batch weights*				
Glaze	Na_2O	MgO	ZnO	Al_2O_3	SiO_2	Soda Feldspar	Greecian Magnesite	Zinc Oxide	Tenn. Ball Clay No. 1	Flint
58	.3⅓	.3⅓	.3⅓	.4⅓	2.2	68.37	10.96	10.57	10.10	.....
59	"	"	"	"	2.5	63.88	10.24	9.87	9.43	6.58
60	"	"	"	"	2.8	59.94	9.60	9.26	8.85	12.35
61	"	"	"	"	3.1	56.45	9.05	8.72	8.33	17.45
62	"	"	"	"	3.4	53.34	8.55	8.25	7.88	21.98
63	"	"	"	"	3.7	50.56	8.10	7.82	7.47	26.05

SERIES XIII.

Formulae						Batch weights				
Glaze	Na_2O	MgO	ZnO	Al_2O_3	SiO_2	Soda Feldspar	Greecian Magnesite	Zinc Oxide	Tenn. Ball Clay No. 1	Flint
64	.3⅓	.3⅓	.3⅓	.5	2.3⅓	64.06	10.27	9.90	15.77	.....
65	"	"	"	"	2.6⅓	60.10	9.63	9.29	14.79	6.19
66	"	"	"	"	2.9⅓	56.59	9.07	8.75	13.93	11.66
67	"	"	"	"	3.2⅓	53.48	8.57	8.26	13.16	16.53
68	"	"	"	"	3.5⅓	50.68	8.12	7.83	12.48	20.89
69	"	"	"	"	3.8⅓	48.17	7.72	7.44	11.86	24.81

These glazes were applied to bone dry stoneware trials and fired to cone 8. They were taken from the kiln while still quite hot. None of them show any signs of crazing. There is very little difference in the whiteness of the members of the two series. All are as opaque and white as a good tin enamel. Nos. 58 and 64 are a little dull. Glossiness increases with increase in SiO_2. The glossiness of Nos. 60 to 63 and 66 to 69 are very good and in this respect will compare favorably with the majority of stoneware glazes on the market and are far superior to them in whiteness. All five pieces of No. 62 are especially good. All members of Series XII have a slight tendency to bead where the glaze is too thick. The glazes do not show any tendency to pull away from the corners and edges. The small beading tendency can be overcome by the addition of borax.

In Series XIII in which the Al_2O_3 is increased the beading has increased a little. The glazes do not appear to be quite so fusible. Otherwise they are good.

In order to compare the opacifying effect of MgO with that of ZnO, the following series was prepared by the class in glaze making in their regular laboratory work. In this series (Series XIV) a glaze of the Bristol type was selected for the first member. In each succeeding one 0.1 MgO replaces 0.1 ZnO, all other members remaining constant.

SERIES XIV.

Formulae							*Batch weights*					
Glaze	K_2O	CaO	ZnO	MgO	Al_2O_3	SiO_2	Potash Feldspar	Whiting	Tenn. Ball Clay No. 1	Greecian Magnesite	Zinc Oxide	Flint
H-1	.3	.2	.5	.0	.5	4.0	167.1	20.0	51.6	....	40.5	128.0
H-2	"	"	.4	.1	"	"	"	"	"	8.4	32.4	"
H-3	"	"	.3	.2	"	"	"	"	"	16.8	24.3	"
H-4	"	"	.2	.3	"	"	"	"	"	25.2	16.2	"
H-5	"	"	.1	.4	"	"	"	"	"	33.6	8.1	"
H-6	"	"	.0	.5	"	"	"	"	"	42.0	....	"

These glazes were applied to small bone dry stoneware crocks and fired to cone 7 in 25 hours.

There is but little difference in the appearance of the members of this series. If anything, H-6 is a little the whitest and smoothest in texture. No bad defects appear. The conclusion which we may draw from the appearance of the trials is that MgO is at least equally as good an opacifier as the same molecular quantity of ZnO.

DISCUSSION.

Mr. Stull: Referring to the trials will say that I have brought only two, No. 35 representing the most promising enamel of last year's work and No. 62 which is the most promising one to date. You will notice that No. 35 is a sort of ivory color and matures altogether too low for stoneware. The trials were nested, and happened to touch at this point (indicating) where a bubble formed, hence this bubble near the rim is not really a defect of the glaze in itself. You will notice that the enamel is badly crazed, and has a little tendency to flake though not bad enough to be serious. No. 62 is a member from Series XII. You will notice in the bottom where the glaze is thick, it beaded in one spot and partially healed over again. Those who have had experience in Bristol glazes will agree with me that the beading is not bad, since no "dope" was added to these glazes to prevent it.

There is a great field open for investigation to determine the opacifying effects of different materials. We have evidence that magnesia is a good opacifier; a good grade of magnesite when properly used in conjunction with zinc oxide will give whiter and glossier effects than the regular type of Bristol glaze.

Mr. Purdy: Those of us who have had experience along this line note with interest the discussion of the opacifying effect of Na_2O as against K_2O, and Mgo as against CaO, in conjunction with zinc.

Mr. Jackson: In regard to the trial passed around, I notice two temperatures mentioned, for instance, cone 01 and cone 8. I am not very familiar with the stoneware business, but I would like to ask whether it is customary to have two fires, a biscuit and glost? Do I understand that the piece going around had a previous biscuit fire?

Mr. Stull: No, sir.

Mr. Purdy: There is only one part of the country that I know of where they use two fires, and that is in the West where they have clays of enormous shrinkage.

Mr. Jackson: Is it practicable and customary to make stoneware as low as 01?

Mr. Purdy: It is not customary; it might be practicable.

Mr. Stull: I am sure there is no true stoneware made in this country as low as 01; but I am sure that terra cotta is made even as low as cone 05 where a slip and enamel are applied to the bone dry ware and matured in one burn, which is a much more difficult problem.

Mr. Purdy: Bristol glaze type?

Mr. Stull: No. sir; an underglaze coating or slip, and white tin enamel or glaze applied over it and all matured in one burn. If it can be done on large pieces, I do not see why it could not be done on small pieces.

Mr. Purdy: Is this over-spray a raw leadless glaze?

Mr. Stull: No sir, a raw lead glaze not a leadless glaze.

Mr. Purdy: That is another question. I do not call that a Bristol glaze. We must be careful to keep Bristol glaze apart from lead glazes because it has different properties.

Mr. Jackson: The point I was getting at is how large a field the one-fire proposition covers so far as a stoneware body is concerned. I do not call any glaze carrying boric acid a Bristol glaze.

Mr. Purdy: You are wrong.

Mr. Jackson: That is the idea I had. Is the boric acid fritted?

Mr. Stull: Yes, sir, it is in series ten and eleven.

Mr. Jackson: I would like to ask Prof. Orton if I am right in what I said. When a glaze carries boric acid fritted in it, can it properly be called a Bristol glaze?

Mr. Orton: It does not meet the idea of a Bristol glaze that I have been teaching. A Bristol glaze is supposed to be a raw glaze. However, this glaze under discussion might be a type which we could afford to use in place of the old raw Bristol glaze. I do not know about that.

Mr. Jackson: That is as I understood it. The glaze at the top of the list on the blackboard is of the Bristol glaze type as I understand it.

Mr. Orton: It is a little too high in silica for a typical Bristol glaze.

Mr. Stull: I am afraid a great many are of the opinion that this work is along the line of Bristol glazes. That is not the line of inquiry, but a cheap enamel for stoneware as indicated by the title on the program. The main object of the investigation is to produce a cheap enamel for the lower grades of ware which will be a fairly good substitute for tin enamel; not only for stoneware but for other types of ware maturing at lower temperatures. That does not confine the investigator to one type of glaze. It is a broad field to work in. I am sorry I have not been able to do more work in this line of experimentation.

Mr. Fuller: What do you mean by "dope" to keep the glaze from crawling?

Mr. Stull: Nearly all stoneware glazes have a tendency to crawl or bead because they are highly viscous. In order to prevent this crawling it is customary for potters to use such materials as plaster of paris, borax, carbonate of soda, or some other soluble salt in their glazes. Exactly what action these soluble salts have upon the glaze has not been definitely determined. My opinion is that in the case of borax and carbonate of soda, these materials not only serve to hold the glaze to the bone dry body after dipping but also fuse in the early stage of burning forming a sticky matrix which prevents the glaze from curling up, which precedes beading.

Mr. Stephani: I would like to say that I have had some experience in the terra cotta line with beading and crawling, and my impression is that there are two kinds. We get one by getting the slip or glaze too heavy on the ware and the consequence is one or the other cracks in drying before it goes into the kiln, and when the glaze begins to fuse it beads and crawls; and in the other case we get an effect which does not appear before it goes into the kiln. I think manufacturers, as a rule, for the first kind of beading, use a material something like calcium sulphate, and some use glue to hold the glaze together in drying, making it tougher. For the second kind, the kind happening in the kiln and which does not show up in the drying, boracic acid is used; or, in a terra cotta glaze the ZnO is reduced with MgO. The latter fault is due to imperfect glaze, while the former can be overcome mechanically, i. e. by applying the underslip or glaze thinner.

Mr. Fackt: May I ask Mr. Stephani whether he has used Cornwall stone in place of the feldspar to prevent the crawling and cracking which he speaks of as happening before the ware goes into the kiln?

Mr. Stephani: I never used Cornwall stone in any glaze; but I find the best way to overcome that effect is by remedying the underslip, or putting less of it on the ware.

Mr. Miller: Mr. Stull tells us he finds an improvement in color by substituting magnesium for tin.

Mr. Purdy: The substitution of magnesium for what?

Mr. Stull: An improvement in color by substituting magnesium oxide for zinc oxide. It does make a little difference in the fusibility. Glazes containing MgO are not quite so fusible as glazes containing ZnO, other things being equal. Dr. Simonis, in his work on cones, in which he used magnesium oxide, points out that the action of the MgO in the cones is to hold the cones up to a certain point when the fusion is comparatively sudden. It is claimed for that reason that they are better indicators of temperature than the regular Seger cones. We are getting more light all the time as to the action of MgO in ceramic mixtures. In fact, we do not yet know all of its possibilities. The magnesite which I used was rather a pure variety obtained from the Foote Mineral Company. I am told that a good variety of the Grecian magnesite is delivered in New York for about twenty-four dollars a ton. If it can be used successfully it will cheapen enamels wonderfully and fill a long felt want for the lower grades of ware.

Mr. Frink: One thing has occurred to me in regard to this discussion of magnesia. Magnesia is used in glass to some extent, usually being found as an impurity in the lime, and experiments have been made which show that the viscosity is very much reduced thereby.

Mr. Purdy: The viscosity is reduced?

Mr. Frink: Yes. That bears out what the gentleman has said. When the temperature rises to a certain point, liquefaction is reached more rapidly. Does not the similar action of borax account for the beneficial results of this material in the case of crawling or beading, because of the filling of the interstices with liquid?

Mr. Purdy: Was it used in a small pot or a big batch?

Mr. Frink: I have experimented with it in tank of capacity of 600 tons, and also with quantities of fifty or sixty pounds.

Mr. Purdy: The viscosity seemed to be the same in both instances?

Mr. Frink: Yes.

Mr. Purdy: What was the effect of magnesia on devitrification?

Mr. Frink: That seems to vary according to conditions, under which it is melted. If melted under a high reducing flame devitrification takes place slowly; but under a high oxidizing flame it takes place rapidly.

Mr. Purdy: Is that peculiar of your magnesium glasses or is it true also of lime glasses?

Mr. Frink: Yes; it is also true as to lime glasses; but with the magnesium glasses it is particularly so and I attribute it to the more liquid condition. That is my theory.

Mr. Purdy: We have to have equivalent of devitrification to have opacity.

Mr. Frink: Yes; and I imagine if you put that under oxidizing conditions you will get that more rapidly.

Mr. Purdy: I will ask Mr. Stull if magnesium in the form of light, fluffy oxide has the same effect as when introduced as magnesite?

Mr. Stull: I have never used the light commercial magnesia only in a fritt on one or two occasions, and have never made any comparisons between it and the mineral magnesite. Commercial magnesia is comparatively expensive. We can obtain magnesite which will analyze very high in $MgCO_3$, with very little impurity which would cause discoloration. There is a deposit in California which is claimed by some to be better than the Grecian, but the cost of mining it and shipping it east is greater. By a little sorting, a comparatively pure grade can be had as low as thirty to forty dollars a ton.

Mr. Purdy: I asked that question in the interest of Hottinger, Barringer, and Hull.

Mr. Stull: What is the effect of magnesia upon iron color in glass? In series twelve and thirteen Tennessee ball clay was used, yet the glazes do not show any trace of cream color.

Mr. Frink: It is so contradictory in action that I cannot answer the question definitely. We sometimes get one effect and sometimes another. I think this is a matter of oxidizing and reducing conditions. It seems to me you would get better results if steam were thrown into the kiln. It seems you have a condition analagous with that prevailing in a lime kiln. I made some experiments one time, introducing steam into a lime furnace. It was found that devitrification was very much enhanced. There are two forms of devitrification, one due to pressure and the other to oxidation. Pure oxygen will produce devitrification.

Mr. Purdy: I note that Mr. Stull did not draw any conclusions in regard to soda or potash feldspar, as fluxes in these glazes.

Mr. Stull: As yet no experiments have been made in this line to determine that. This will probably be investigated later.

NOTE ON THE USE OF PYROMETRIC CONES.

BY

H. B. HENDERSON, Columbus, Ohio.

It is quite generally known by those accustomed to the use of pyrometric cones that they are very susceptible to sudden increases of temperature and to flashing. They are therefore careful to protect the cones from direct contact with flames by setting them under special hoods or in protected places or by building protecting walls around them.

It is not so commonly known, however, that the cone is just as sensitive to cooling off suddenly, but with the opposite effect. A sudden cooling by opening a port and allowing a stream of cold air to rush in while viewing the cone, or cooling the cone by means of an iron bar in order to see it more clearly, will cause it to stand apparently unaffected at a temperature that would have brought it down under proper treatment.

It is noticeable, however, that the cones that have been fired once and afterward placed in another kiln with raw cones, stand the higher degree of temperature.

Observations point continually to this phenomenon, but a satisfactory explanation of it is still lacking.

NOTE ON THE EFFECT OF THE RATE OF APPLICATION OF HEAT TO CLAYS AND CLAY BODIES.

BY

H. B. HENDERSON, Columbus, Ohio.

A marked difference in shrinkage has been noticed when the same clay or mixture is fired to the same cone at different rates, the slow burn giving a greater total shrinkage than the rapid burn. While the observations are not complete enough to warrant a definite analytical statement, they indicate that shrinkage is proportional to the rate of temperature increase. Moreover, it appears that the bodies reach their maximum shrinkage at a lower temperature in a short sharp fire than in a long slow fire.

This conception being so radically different from the view ordinarily taken concerning shrinkage in the vitrification process, I had hoped to present experimental data, but lack of time for completion of the work compels me to omit it.

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